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The Oxidation of Methane

DISSERTATION

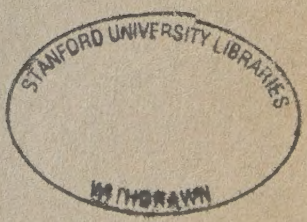
PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

CHARLES FERDINAND RUDMANN, B. A., M. A.

The Ohio State University
1921

Published 1929



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THE OXIDATION OF METHANE

SUMMARIZED RESULTS

The following investigation of the slow combustion of methane indicates:-

1. The applicability of fused quartzware pipettes in slow combustion anlyses as demonstrated by Vilbrandt.

2. An improvement in the preparation of methane by the method of Gladstone and Tribe.

3. Additional evidence for error due to the loss by absorption of methane in the reagents used for the determination of carbon monoxide and unsaturated hydrocarbons.

4. Confirmation of the applicability of sodium pyrogallate, rather than potassium pyrogallate, as an absorbent for oxygen.

5. Satisfactory service of the Dennis Winkler pipette as modified in regard to coil insertion.

6. That while a new type of combustion pipette- the Central Upright Burner- eliminates excessive heating of the capillary junction with the pipette proper, yet, as compared with a slightly modified Dennis Winkler pipette- more care is required in its use and a persistently lower percentage of methane is obtained.

7. A new form of quartz capillary combustion pipette was found to be easily adjusted but proved unsatisfactory in service.

8. Side products of oxidation of methane as occuring in its routine analysis are not formed in sufficient quantity to affect percentage results.

9. As had been previously noted, quantitative combustion of methane is attained with some difficulty.

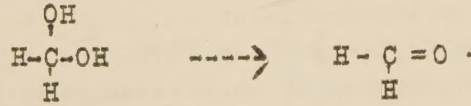
10. Some regularity in the temperature of the platinum coil used in analysis is advisable, to eliminate discordance in much experimental work and to arrive at a standard procedure.

II. INTRODUCTION

Methane is the chief constituent of natural and fuel gases and is also present in mine air. Since mine gas explosions are due to the ignition of methane and air, extensive investigation has been made in this field. A study of methane is also interesting because of the fact that it is the simplest hydrocarbon and serves, theoretically, as the source of formation of organic compounds, by oxidation and substitution. Very little is really known about the oxidation of methane, especially in gas analysis, other than that carbon dioxide and water are formed and the determination of methane in a gas is based upon the assumption that the gas burns completely to carbon dioxide and water. This phase of the topic will be discussed more fully below. The organic chemist has long been interested in the speculation that if one oxygen atom is inserted between one carbon and one hydrogen, thus,

it becomes carbinol or methyl alcohol for which there is at present no adequate source other than the destructive distillation of wood. If this oxidation is continued, a dihydric alcohol derivative of methane is theoretically possible, thus,

but practically, can be expected to automatically dehydrate itself, leaving as the residual compound, formaldehyde, thus,



whose increasing commercial importance is well known and which is mainly derived commercially by the oxidation of methyl alcohol, essentially as just mentioned. If the

oxidation is continued, the simplest organic acid, formic acid, results, thus,

$$H - \underset{H}{\overset{|}{C}} = O \longrightarrow H - \underset{OH}{\overset{|}{C}} = O$$

The present small demand for this acid might reasonably be expected to increase with cheaper means of production, or, if it could be readily be prepared from methane.

With these ideas in mind this problem has been studied from the following viewpoints:

1st. Qualitatively to see roughly what can be produced by various means of oxidation under ordinary gas analysis conditions. (other work is being carried out in this laboratory, using various catalyzers to determine the oxidation products.)

2nd. Precisely, as accurately as possible, so as to be able to measure the influence of various conditions of oxidation upon the nature of the products. This is the main problem of this thesis.

It is well known that the only precise work which has hitherto been done upon the oxidation of methane is that which comes up in routine gas analysis and the methods and technique of this procedure were adopted in studying our problem. In doing so, however, it was early discovered that while gasometric combustion methods, are sufficiently precise for ordinary analytical methods, yet much of interest has been over-looked. It is surprising to find that nowhere in gas analysis literature (altho otherwise well known as possibilities) has anyone called attention to the fact that intermediate products of oxidation such as methyl alcohol, formaldehyde and formic acid could be produced, although such formation, obviously, might affect even analytical results. Thus:

In the complete combustion of methane, there is a contraction of two volumes. Thus:

$$(1)\ CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

The percentage methane is calculated from the CO_2 or from $\frac{1}{2}$ the contraction (Note Dennis Gas Analysis 1913 Ed., 242. "Since, when a volume of methane produces on combustion, one volume of carbon dioxide per equation

(1) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

1 vol. 2 vols. 1 vol. Liquid

The volume of methane in the gas mixtures is equal to the volume of the carbon dioxide formed. Since -

(2) $2H_2 + O_2 \longrightarrow 2H_2O$

2 vol. 1 vol. Liquid

the contraction due to the combustion of hydrogen is equal to 3/2 the volume of hydrogen in the gas mixture. The contraction due to the combustion of methane (equation 1) is equal to twice the volume of carbon dioxide formed. Consequently the total contraction in the gas volume that results when a mixture of hydrogen and methane is burned may be represented by the expression:

Contraction $3/2\ H_2 + 2CO_2$

or $3/2\ H_2 =$ Contraction $- 2CO_2$

or the volume $H_2 = 2/3$ (contraction $- 2CO_2$)

The volume of hydrogen in the gas mixture is therefore found by subtracting twice the volume of carbon dioxide formed in the combustion from the total contraction and taking 2/3 of the remainder.")

If methyl alcohol, formaldehyde, or formic acid, were the products of combustion of any portion of the methane we would have to that extent:

(2) $2\ CH_4 + O_2 \longrightarrow 2CH_3OH$

or (3) $2\ CH_4 + 2O_2 \longrightarrow 2HCHO + 2H_2O$

or (4) $2\ CH_4 + 3O_2 \longrightarrow 2HCOOH + 2H_2O$

In (1) three volumes of original gas mixture contract to one volume, the CO_2 being $\frac{1}{2}$ the contraction.

In (2) three volumes contract to zero volume, as methyl alcohol is a liquid.

In (3) four volumes contract to two volumes or less, since formaldehyde is a gas, but partially soluble in water.

In (4)-formaldehyde readily oxidizing to the acid-five volumes contract to zero, since formic acid is a liquid.

The majorpart of the methane would burn, without doubt, according to equation (1) but the contraction, due to (2) or (4) and probably (3), would be more than double the CO_2 found. Authorities assume that such a contingency means the occurrence of hydrogen in the gas (see previous note) because hydrogen gives complete contraction to water leaving no residual carbon dioxide.

This means two things:

(1). Previous work cannot be depended upon to tell us anything about the products of oxidation of methane under gas analysis conditions, but we must study the whole field ourselves to obtain the answer we seek.

(2). The calculations of all modern precision gas analysis are based upon a total ignoring of simple organic chemical considerations.

III. LITERATURE

To aid in the investigation of the problem, reference was made to the literature for information under two main headings, viz:

1. Products of combustion (or oxidation) of methane.
2. Methods of analysis of methane.

LITERATURE OF THE OXIDATION OF METHANE

The following notes show what various experimenters have thought and found in regard to the oxidation products of methane though their conditions were not the same as occur in gas analysis.

Dixon (J. Chem. Soc., 49 (1886), 107) obtains formic acid (method of testing is not given) when induction sparks are passed thru carbon monoxide and steam. He also states that Traube (no reference given) consider hydrogen peroxide to be produced by the burning of hydrogen and oxygen.

Phillips (Am. Chem. J. 16 (1894), 171) states that in the oxidation of hydrocarbons in a tube in excess of air it is probable that both carbon and hydrogen burn simultaneously to carbon dioxide and water. He explains

that selective oxidation might occur involving the formation of condensation products as:

$$2\ CH_4 + O_3 \text{ ----- } 3H_2O + C_2H_2$$

$$2\ CH_4 + 2O \text{ ---- } 2H_2O + C_2H_4$$

The same author (ibid p-184) states that the oxidation of gaseous hydrocarbons in excess of air involves simultaneously the formation of carbon dioxide and water and only these two.

Bone and Wheeler (J. Chem. Soc., 81 (1902), 535, Chem. News 85 (1902), 137.) in experimenting with methane in glass tubes in a furnace, find that between 300° and 400° C, methane combines with oxygen with an enormously greater velocity than does hydrogen itself under the same conditions. At no stage in the oxidation are they able to detect the formation of such products as methyl-alcohol, formaldehyde and formic acid. Carbon always appears as carbon monoxide or carbon dioxide.

Bone and Wheeler (Chem. Soc., 83 (1903), 1074) as the result of additional experiments under better conditions, show that hydrogen is not produced and final products consisting simply of carbon monoxide, carbon dioxide and steam, prove the transietn formation of formaldehyde as an intermediate product. In one experiment 13% and in another 22 percent of the methane burnt was accounted for as formaldehyde and removed from the sphere of action before being further oxidized. Two distinct and successive changes in the oxidation of methane were concluded, viz:

$$(1)\quad H - \overset{H}{\underset{H}{C}} - H + O_2 \text{ ---} \rightarrow H - \overset{H}{C} = O, \text{ followed}$$

by 2 simultaneous and rapid reactions,

$$(a)\quad H - \overset{H}{C} = O + O_2 \text{ ---} \rightarrow CO_2 + H_2O \text{ (bimolecular)}$$

$$(b)\quad 2H - \underset{H}{C} = O + O_2 \text{ ---} \rightarrow 2CO + 2H_2O \text{ (trimolecular)}$$

Possibly (b) may involve the formation and very rapid decomposition of formic acid, thus:

$$2HCHO + 2\ O_2 \text{ ---} \rightarrow 2HCOOH \text{ ----} \rightarrow 2\ CO + 2H_2O$$

(2) The formation and rapid decomposition of the hypothetical $H - \overset{OH}{\underset{H}{C}} = OH$

$$CH_4 + O_2 \rightarrow H_2C(OH)_2 \rightarrow HCHO + H_2O$$

Such views are said to agree with the facts. Figures are given by Bone and Wheeter from which it was concluded that some intermediate products must have been formed. Their experiements show the formation of formaldehyde but no tests were obtained for methyl alcohol. Experimental evidence is given to show that formaldehyde is not produced according to the equations:

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O$$

$$CO + H_2 \rightarrow HCHO$$

Armstrong (J. Chem. Soc., 83 (1903), 1083) has a theory that the following reaction takes place (no test mentioned).

$$CH_4 + H_2O + O_2 \rightarrow CH_3OH + H_2O_2$$

Bone (Chem. News, 88 (1903), 283.) for combustion of methane uses apparatus in which the reacting mixture can be circulated day and night at a uniform rate, over a surface maintained at a constant temperature of about 300° and then thru absorbing arrangements. The reactions are as in the preceding article by Bone and Wheeler. The velocity of these low temperature reactions will increase rapidly as the temperature rises and aldehyde formation will occur as long as the aldehydes can exist. The production of formaldehyde in the oxidation of methane will only be limited by the temperature at which formaldehyde is incapable of existence. No alcohol has been found.

Trillat (Compt. rend., 138 (1904), 1613) relates experiments showing that in all laboratory combustions of various substances such as wood, paper and hydrocarbons, formaldehyde is produced although in very small amounts. The formaldehyde was detected by the color test with dimethylaniline.

Bone (Eng., 85 (1908), 314.) concludes that the results of exhaustive study of slow combustion of methane ethane, ethylene and acetylene attemperatures ranging

from 250-400°C. afford decisive evidence against any preferential combustion of one element over the other. Unstable intermediate products, such as, aldehydes and alcohols, are formed and in turn break down to the final products. Bone has obtained experimental evidence (omitted in article) that in explosive combustions a similar sequence takes place.

Researches at the University of Manchester by Bone (Chem. News, 97 (1908), 196) on the slow combustion of methane, ethane, ethylene and acetylene between 250 and 400°C., afford decisive evidence against the preferential burning of carbon and hydrogen. Large quantities of aldehydic products are said to have been isolated, and the balance of evidence was in favor of the "hydroxylated" molecules formed (and decomposed at high temperatures) in the combustion of a hydrocarbon under the conjoint influence of water and oxygen.

$$CH_3 \cdot CH_3 \longrightarrow CH_3 \cdot CH_2OH \longrightarrow CH_3CH(OH)_2 \longrightarrow CO_2 + H_2O + H \cdot CHO \longrightarrow HCOOH \longrightarrow CO_2 + H_2O.$$

As the temperature rises the intermediate products become more and more unstable, and to an increasing extent decompose into simpler products, which then undergo independent oxidation, as, formaldehyde to carbon monoxide and water.

Bone and coward (J. Chem. Sox., 93 (1908), 1197) examine various theories on the modes of decomposition of methane, ethane, ethylene and acetylene. By experiment methane is found to be the principal product of decomposition of the other three, especially above 800°C. It decomposes for the most part into carbon and hydrogen.

Meunier (Bull. soc. chim., 3,4e serie (1908), 569), in experiments on methane with a hot disk, found some unburned gas containing aldehyde, alcohol and carbon monoxide.

Wieland (Ber., 45(1912), 3515) detected formic acid in the methane flame. The flame was allowed to melt ice and the resulting water contained formic acid. This was neutralized with a few drops of barium hydroxide, evaporated on the water bath and finally to dryness after fil-

tration of the separated carbonate. The residue though small in amount gave with a silver salt, a decided test for barium formate. He attributes its formation to the decomposition of the methane into carbon and hydrogen, the carbon with water giving carbon monoxide, the source of the formic acid.

Hauser and Herzfeld (Ber.,(1920), 17) use the reaction between methane and ozonized air forming formaldehyde as an excellent means for detecting methane. Sufficient formaldehyde is formed to give an odor and after absorption in water its presence is confirmed by the morphine sulfuric acid reaction.

Winter (Brennstoff Chem., (1920), 17) reports complete combustion of a mixture of pure methane and air containing 5-9.2 per cent methane. Incomplete combustion occurs in a mixture containing 9.2 - 14 per cent methane. In addition to carbon dioxide, water and hydrogen the residues may contain carbon monoxide. Winter also favors the idea as advanced by Armstrong (J. Chem. Soc., 83 (19031, 1088 and Wheeler (Proc. Chem. Soc., 19 (1903), 191) that in the combustion of methane, the hydroxylation of the molecule takes place while aldehydic intermediate products result, viz:

$$CH_4 + O_2 \longrightarrow CH_2O + H_2O$$

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

$$2CH_2O + O_2 \longrightarrow 2(HCOOH) \longrightarrow 2CO + 2H_2O$$

$$2CO + O_2 \longrightarrow 2CO_2$$

Formaldehyde and formic acid are said to be proven (evidence not given) as intermediate products of the slow burning of methane. Wieland's work (Ber., 45 (1912), 2606) was confirmed and extended. As noted previously Wieland attributed the formation of formic acid in the methane flame to the presence of carbon monoxide. Winter discusses the formation of carbon monoxide in the presence of insufficient oxygen for complete combustion. He also gives experimental evidence showing that the percent methane burned to carbon dioxide and water increases with the increase in the ratio of oxygen to methane.

Wartenberg and Sieg (Ber., (1920), 2202) write that Bone and Wheeler (J. Chem. Soc., 83 (1903), 1074) state that 13-22 per cent formaldehyde forms by the reaction $CH_4 + O_2 = CH_2O + H_2O$. Carbon monoxide and oxygen with moisture form formic acid which decomposes to carbon dioxide and water. Water forms hydrogen peroxide with oxygen and hydrogen peroxide decomposes to water and oxygen. They write that with methane formaldehyde and water are the principal products and from these carbon monoxide and carbon dioxide result.

Glock (Chem. Zeit., (1900), 197; Zeit. angew. Chem., (1900), 227) passes methane mixed with air over glowing platinum. According to Coquillon formic acid results, but, neither methyl alcohol nor formaldehyde. The discoverer has found that the goal is reached if, instead of platinum, milder contact substances such as copper, asbestos or pumice be used. As an illustration, methane and air in equal volumes were led over copper at a dark red glow (600°C.). The product was cooled and washed with water, mixed with air, led over coper again, etc., until no more methane remained. Methyl alcohol and formaldehyde were obtained from the water.

Lance (Eng. patent, 7297 (1906)) deals with the making of methyl alcohol from methane. He uses hydrogen peroxide, with or without ferrous sulfate or monopersulfuric acid, or with monopersulfuric acid alone.

The Sauerstoff and Stickstoff Industrie Hausmann and Co., (Ger. patent, 214,155 (1908)) have a patent by Unruh (U.S. patent 891,753) which deals with the production of formaldehyde, methyl alcohol and formic acid from methane mixtures with air or oxygen. The gases are passed over granulated copper at 600°C. If fatty substances are used as a contact mass, as for example, tan bark, the process may be carried on at 30-50°C.

A German article (Chem. Zeit., (1908), 894) gives some extravagant appearing information concerning the production of methyl alcohol from gas at Fairmont, W.VA.

Kunhein and Cp. (D.R.P. 205774-Jahres Bericht der Chem. Technologie 55 (1909), part 1, 399) claim that rapid cooling of methane or methane containing gases results in incomplete combustion of methane and the formation of formaldehyde.

Fernecke's method (U.S. patent, 1038,547 (1912) consists in heating a stream of methane and air to ignition. An inner stream (excluded from the outer) of a similar mixture is thereby oxidized to formaldehyde.

Verein fur Chem. Ind, in Mainz has a patent (Ger. 286,731 Aug. 1913); C.A.1916, p. 1911) for the preparation of formaldehyde from methane. A mixture of three parts methane and one hundred parts moist air is conducted in a closed system over a contact substance, such as copper or silver or both at a temperature of from 150-200°.

Bancroft (Trans. Am.° Electrochem. Soc., 32 (1917), 465) has a detailed discussion of contact catalysis and fractional combustion and states that it should be possible to obtain all intermediate stages from complete combustion of methane to complete combustion of hydrogen in a mixture of these gases by suitable selection of a catalyst. The specific effect of the catalyst probably disappears at high temperature as the reaction occurs so rapidly in a gas phase, that the equilibrium reached will be that of the gas phase, and not that of the catalyst.

Blackmore (U.S. patent, 774,824; Am. Gas Eng. J., 108 (1918), 489) claimed to obtain 118 pounds formaldehyde upon passage of 1500 cu. ft. of methane over certain metallic oxides.

Muller (Ger. patent, 207,380, (1918); C.A.(1919), 1133) states that by the use of a catalyst made from croceocobalt nitrate (heated at 150° in nitrogen) up to 8% formaldehyde may be obtained from methane and oxygen.

Bailey (J. Chem. Soc., (1920), 1, 213; U.S. patent, 319,748) has a patent for obtaining oxidation products including formaldehyde by passing methane or natural gas

mixed with twice its volume of nitric oxide with sufficient oxygen or air to form nitrogen peroxide through an inert tube heated to redness.

There are several references to the use of silver as a catalytic agent in the preparation of formaldehyde from methyl alcohol. Thomas (J. Am. Chem. Soc., 42 (1920), 867) obtains a much better yield of formaldehyde from methyl alcohol at 400° by the use of silver rather than copper or gold.

LITERATURE ON THE ANALYSIS OF METHANE

The methods of combustion of gases for analytical purposes fall into three classes, viz.,

1. Explosion method.
2. Actual flame combustion methods.
3. Combustion tube or capillary methods.

The explosion method was the first one used and is still used for approximate analysis though it has been discarded by the majority of investigators, especially for accurate work. The measured amount of gas and oxygen or air in proper proportion (Bunsen, J. prakt. Chem., (1907), 212; Burrell, J. Ind. Eng. Chem., 5(1913), 181) are mixed in the explosion chamber, the level bulb adjusted to produce a diminished pressure; and the explosion produced by sparks passing between electrodes sealed into the top of the pipette.

The following objections are given by investigators as sufficient cause for discarding the explosion method:

(a). Additional time and manipulation are necessary to mix the gases.

(b). Control of the force of explosion is difficult.

(c). If the explosion is too violent, the apparatus is either broken or large amounts of oxides of nitrogen form.

(d). If the explosion is insufficiently violent, combustion is incomplete.

(e). Exceptionally tight connections must be maintained on the pipette to withstand the pressure of the explosion. If rubber tubing be used, there is a great tendency to leakage: if glass stopcocks are used, the

inflexibility tends to greater percent destruction of the apparatus.

(f). Many gases, mine gas for example, do not contain explosive gases in sufficient quantity to form an explosive mixture. Hence, to produce an explosion, hydrogen must be added, requiring additional time and manipulation.

(g). To avoid too violent an explosion, but a small quantity of gas can be taken for analysis. This lessens the accuracy, for any small error is increased several times in the final percentages.

No work whatever was done by the writer with the explosion method.

CAPILLARY METHODS

Drehschmidt (Ber., 21 (1888), 3250) says that the methods recommended in Winkler's book, viz., combustion by means of the palladium expiral or copper oxide, require oxygen in dilute form to avoid explosion. He adds that Orsat (Cl. Winkler, Industriegase Bd. 2, 198) had obtained some results by the use of a platinum capillary method, but they were rather uncertain, also that, according to Winkler, the permeability of the glowing platinum must be considered, and the use of oxygen instead of air in such a method easily leads to explosion. Drehschmidt's first platinum tube, 20 cm. long, 1 mm. diameter and 0.3 mm. bore was heated with a Bunsen burner on passage of the gas. No explosion resulted but the tube showed a tendency to leak. A tube 2 mm. in diameter and 0.7 mm. bore was then used. No leaks were found but explosions resulted with methane especially, though not always with hydrogen. These were avoided by almost closing the opening with palladium wires put into the tube. Tests showed diffusion to be inconsiderable. Combustion was complete after three or four passages of the gas through the tube heated to a bright redness (a dark red glow being insufficient for complete combustion).

Bleier (Ber., 30 (1897), 697) shows two forms of explosion tubes. In an enlargement of capillaries are sealed two platinum wires almost touching each others.

The capillaries are filled with water, the current turned on and the gas mixture allowed to enter. In a third type the horizontal capillaries open into an enlargement closed at the bottom with a rubber stopper. In the enlargement is a platinum coil, connections being made through the stopper as is the case with the Dennis Winkler combustion pipette. The apparatus is of glass and no dimensions are given.

Wencelius (Chem. Ztg., (1902), R2, 200) uses a 0.7 mm. bore platinum cappillary tube provided with water coolers, for the analysis of combustible gases.

Kuntze (Chem. Ztg., (1910), 830) uses a form of Orsat apparatus and a platinum capillary in the form of a U tube. He says that a quartz tube may be used.

Hempel (Gas Analysis, 1910 Ed., 139) says that reliable results may be obtained by explosion and capillary combustion methods, but that the platinum capillary tube containing platinum wire is undoubtedly the simplest form of combustion apparatus for technical purposes. Another advantage is that the capillary so reduces the temperature of the gases passing through it, that the combustion temperature of nitrogen can not be reached.

Hempel (Zeit. Angew. Chem., (1913), 2, 638) finds that methane is not completely burnt in the Drehschmidt capillary when an ordinary burner is used, but only when a small blast lamp is used. He shows that the platinum capillary can be advantageously replaced by a quartz capillary almost filled with platinum wire. With the quartz tube in a little oven heated by a small blast lamp and with slow passage of the gas, no explosion occurs. The quartz must be the transparent variety as the milky quartz is not gas tight. To avoid mercury oxide formation as in the combustion pipettes Hempel recommends the use of a transparent quartz tube provided with an electrically heated platinum spiral.

This quartz tube is 13.5 cm. long and 3-4 mm. internal diameter and united by rubber tubing to two glass capillaries of the same external diameter. These capillaries of the same external diameter. These capillaries

are drawn out and partly extend into the quartz tube. Between them is a wound spiral of 0.2 mm. and 18 cm. long platinum wire. This extends through the capillary tube and is melted into and through the capillary at the ends beyond the rubber connection. Up to 80 cc. gas may be brought to burn without burning measurable quantities of nitrogen if the gas is passed through slowly. According to the abstract in the J. Soc. Chem. Ind., 1912, 921, these capillaries are of quartz and the platinum spiral is connected to two platinum wires sealed into the capillaries. According to Shenstone, Methods of Glass Blowing, p. 87, it is not possible to seal platinum wires into silica tubes.

Levy (J. Chem. Ind., 31 (1912), 1153) describes an apparatus for the examination of mine air but which can be employed for ordinary gas analysis. The gas enters a quartz tube of 0.5 mm. bore and slightly curved where it joines a straight tube containing a platinum wire sealed into the tube with molybdenum leads. This tube is of 1.0 mm. bore and is surrounded by water. After coming in contact with the white hot platinum wire, the burnt gas passes out through a tube similar to the entrance tube.

Winkler (Dennis Gas Analysis, 191 Ed., 155) placed water jackets at the ends of a platinum capillary 100mm. long 2.5-3.0 mm. in external diameter and 0.7 mm. internal diameter. The tube is bored or drawn to avoid a leakage from lapweld tubes. The chief objection (of Dennis) to the Drehschmidt tubes now (1913) on the market lies in the fact that they begin to leak after having been in use but a comparatively short time.

Mathers and Lee (Chem. Eng., 17 (1913), 159) pass the gas residues after addition of oxigen through a heated (by Bunsen burner) quartz tube which contained pieces of scrap platinum. This tube was 30.5 cm. long, 3.38mm. bore 3.317 cc. capacity and a void of 2.795 cc. after 11.188 gm. platinum had been placed inside. The authors claim several advantages:

Platinum tubes are expensive and deteriorate in use.

Quartz tubes are not easily broken and are cheap, while the platinum used is scrap material.

No metal or other oxidizable material is in the quartz tube.

Small cracks in glass tubes or leaks around the rubber stoppers cause serious errors. There is little chance for leaks in quartz tube apparatus.

The temperature in the quartz tube may be made high enough to insure complete combustion.

However, a correction must be made for the carbon dioxide remaining in the quartz tube after the combustion, although they think that this disadvantage may be overcome by the use of a smaller capillary tube whereby a correction is unnecessary.

White (Gas and Fuel Analysis, 1913 Ed., 49) modifies the quartz arrangement of Hempel. At each end of a transparent quartz tube 4 mm. internal diameter and 125 mm. long are glass capillary tees connected to it by rubber tubing. Through each tee runs a stout nickel wire connected by a spiral of fine platinum wire. The nickel wires are sealed into the glass capillaries by sealing wax drawn into the enlarged end of the capillaries. The apparatus may therefore be readily repaired if the platinum wire becomes burnt out. The nickel wire should almost fill the capillary tube of one mm. bore and by cooling action help to prevent any explosion from flashing back into the burette.

Levy (Zeit. Angew. Chem. (1914), 2, 638) criticises the Drehschmidt pipette unfavorably in that it requires heating from outside, thus allowing no exact temperature regulation. His own apparatus described above, has exact heat regulation due to the electrically heated platinum spiral, while the passage through the quartz capillary guarantees complete burning.

Smith (Gas World, 71 (1919), 379) passes the proper mixture through a platinum capillary tube into an additional absorption pipette filled with water. The platinum tube being raised to a white heat by a Bunsen burner. The mixture is then returned and passed through

the tube three times, when all the combustibles are burnt completely. The capillary tube is five inches long, 1-16 inch external diameter, the bore being as fine as a hair, and mounted into brass ferrules, the external diameter of which is the same as the glass branched capillary tube to which it is attached.

Weaver and Ledig (J. Ind. Eng. Chem., 12 (1920), 368) claims that there is considerable advantage in the use of a combustion capillary for the determination of small amounts of combustible gas. They say that Levy's apparatus is very satisfactory in service, but the coil can not be replaced if broken or burnt out and the device is expensive and difficult to obtain, while a similar capillary in which the lead wires pass through rubber stoppers is unsatisfactory. They object to the capillaries of Hempel and White because of the rubber connections between the quartz tubes and the glass tubes which carry the lead wires. The former is also hard to put together in good form, and must be rebuilt when either the wire or the rubber tubing requires replacement. Three forms of combustion capillary apparatus made of pyrex are described. The portion containing the coil has an inside diameter of about 3 mm. and the connecting capillary tubing has an inside diameter of about 1 mm. The platinum wire is made into a coil and drawn into place by the use of another wire. Connections with the current are made by the use of soft glass caps fastened on the pyrex with Khotinsky cement. The caps are placed so that they are at angles to the part of the tube containing the coil.

Ott (J.f. Gasbel., 63 (1920, 198) uses a quartz capillary filled with platinum wire. He finds this to be cheaper than the usually employed platinum capillary and also completely air tight, whereas the latter is so only to an limited extent. The quartz capillary is 240 mm. long, 1 mm. in diameter and with walls 2 mm. thick. The tube is filled with three platinum wires extending about 20 mm. beyond the capillary on each side into glass capillaries. This was heated from below. Ott says that milky molten quartz proved to be completely air tight at a glowing temperature (contrary to Hempel

as noted previously). On the other hand it is necessary to activate the platinum, best by treatment with aqua regia.

In the same discussion (p.269) Ott gives the result of comparative tests using a quartz capillary and a thick walled platinum capillary. While tight in the cold, the latter was found to be permeable to hydrogen at glowing temperatures. No constant value could be obtained in the combustion of a known water gas mixture. He thinks that this volume decrease due to the porosity of platinum, has not been especially noted previously because of the fact that readings were made without good manometer control.

CAPILLARY COMBUSTION WITH COPPER OXIDE

Under the head of capillary combustion might be included analyses in which catalytic or oxidizing agents are used, as copper oxide, palladium asbestos and palladium black. During the last few years a number of favorable references are given to the use of copper oxide especially for use in the fractional combustion of hydrogen and carbon monoxide. A brief mention of the copper oxide method as found in the literature outside of texts is given.

Jager (J. Gasbel., (1898),41) and Uhlig (J. Soc. Chem. Ind., 29(1910), 196) determine hydrogen at 270° and methane at full red heat of the copper oxide in glass tubes.

Knorre (Chem. Ztg., (1909), 717) and Uebbelodhe and de Castro (J. Gasbel., 54 (1911), 810) follow the method of Jager but use quartz tubes instead of glass.

Taplay (J. Gasbel., (1912), 217,285) uses a copper oxide tube heated at 270° for hydrogen and at 850° for the methane combustion.

Worrel (Met. Chem. Eng., 11, (1913), 245) after using a glass tube to contain copper oxide substitutes a silica tube heated to 250-260 for hydrogen and red heat for methane.

Dennis (Gas Analysis, 1913 Ed., 200) determines hydrogen in soft glass tubes heated to 270° C and then passes the paraffins into the slow combustion pipette, as distinct from the methods given above.

Terres and Manguin (J. Gasbel., (1915),8) and Wibaut (Chem. Weekblad, (1914), 11) make use of the copper oxide method but Wibaut mixed cerium oxide with the copper oxide and claims better results.

Taplay (J. Gas Lighting, (1915), 870,933) describes a somewhat different apparatus in which is a fused silica combustion tube containing the oxidizing material-copper oxide- in the form of a rod, supported in the center of the tube.

Taylor (J. Ind. Eng. Chem., 6, (1914), 845) obtains the percentage of paraffin hydrocarbons by use of a heated platinum spiral, after determining hydrogen over copper oxide in a glass tube.

Burrell and Oberfell (J. Ind. Eng. Chem., 9 (1917), 288) state that the use of copper oxide in the determination of hydrogen and carbon monoxide in gas mixtures has given much better satisfaction than methods demanding the use of acid and ammoniacal solutions of cuprous chloride for the determination of hydrogen. They believe that the method should be used more widely than it is. The copper oxide is contained in a glass U tube maintained at a temperature of 275-300° C. for burning carbon monoxide and hydrogen. The paraffin hydrocarbons are burned in a slow combustion pipette.

Suydam (J. Ind. Eng. Chem., 9(1917), 734) uses a quartz U tube but otherwise there is no change from the method of Burrell and Oberfell; similarly, Jones and Neumeister (Chem. Met. Eng., (1919), 734) employ a pyrex U tube.

Ott (J. Gasbel., (1919), 62,89) states that there is uncertainty in fractional combustion when copper oxide is used in consequence of the dissociation of copper oxide to copper and oxygen, which can be eliminated by subsequent repeated passages of the gas over the material in a quartz tube which is maintained at a low red heat.

Copper oxide does not appear to be suitable for gas analysis in which the carbon monoxide formed by combustion is measured.

USE OF PLATINUM WIRE OTHER THAN IN CAPILLARY COMBUSTION

Coquillon (Compt. rend., 83(1876),394; 84(1877),458) proposed to estimate small amounts of hydrocarbons in the air from mines by placing within a pipette a spiral of platinum or palladium wire. The mine air was introduced into the pipette, the spiral heated to redness and amount of combustible gas being below the explosive ratio, the hydrocarbons were to be gradually burned. He recommends that for technical gases where there is danger of explosion the platinum spiral beplaced in a small bulb blown in the capillary tube between the burette and pipette. The misture of gas and air was measured in the burette and then passed through the capillary over the glowing spiral-the capillary tube being supposed to be adequate to prevent any explosions from flashing back into the burette.

Winkler (J. Soc. Chem. Ind., (1889), 570) modified the method of Coquillon by using the Hempel absorption pipette for solid reagents with water or KOH over which the gas was burned, the carbon dioxide being absorbed immediately.

Dennis and Hopkins (J. Am. Chem. Soc., 21 (1899), 398) modified the Winkler pipette chiefly by adding a level bulb connected by a rubber tube and using mercury as the confining liquid.

Voldere (Chem. Ztg., 31 (1907), 1296) submerges the pipette in water.

M. Bretschger (Treadwell and Hall, Quantitative Analysis, 1915 Ed., 795) sealed the platinum spiral through the walls at the top of the pipette to get away from leakage around the rubber stopper.

Later Dennis (Gas Analysis, 1913 Ed., 148) modified his pipette to take care of the excess oxidation of the iron wire by using 'mercury cup' electrodes.

The Haldane apparatus (Bureau of Mines, Bull. 42, (1913) 17) is used primarily for the analysis of mine

gas where the percentage of methane is around 1.0 per cent.

Burrell (ibid. p. 42) developed a form of combustion pipette to use on a common train with absorption pipettes. This consists of a bell shaped vessel, slightly elongated with a short upright capillary at the top, the lower opening being as wide as the remainder of the pipette.

Scott (J. Ind. Eng. Chem., (1909), 118) recommends a long tube in which is placed a platinum wire running the length of the tube, claiming several advantages, among them being that of complete combustion. No supporting data is given.

Burrell (U.S. pat., 1, 176,199 (1917)) has a Universal pipette consisting of a U tube, the combustion arm of which is metal, the other a graduated glass tube. The contraction on combustion is noted by the fall of liquid in the graduated tube.

The Anderson pipette is pear shaped, the small part serving as the top for the entrance if the gases. Completeness of combustion (J. Ind. Eng. Chem., 11 (1919), 299) is indicated by the use of a side arm extending from the level bulb connectinn up as high as the top of the combustion pipette.

Weaver and Ledig (J. Ind. Eng. Chem., (1920), 368) use a pyrex glass pipette at the top of which are two side tubes. Through these tubes a platinum wire is strung and the tubes are closed and made air tight by the use of small glass caps and Khotinsky cement.

Various experimenters have made slight modifications in the set up of the Dennis Winkler apparatus but the general principles have remained the same. In use oxygen or air is measured and passed into the combustion pipette. Then the gas is measured, the current sent through the platinum to produce a red to white heat and the gas slowly passed in. After combustion the current is turned off, the pipette allowed to cool and the contraction measured and the carbon dioxide absorbed. The cooling may be hastened by a current of air or water.

According to some authors the gas may be first introduced into the pipette and oxygen or air then passed in from the burette. Dennis (Gas Analysis, 152) in a discussion of the apparatus writes that this method is not suited to the combustion of acetylene because the hot spiral causes decomposition of the gas with deposition of solid carbon.

Also, according to Dennis and Hopkins (J. Am. Chem. Soc. 21 (1899), 398) if the gas is passed in first, methane, in the presence of heated platinum and water, may form carbon dioxide and water.

Taylor (J. Ind. Eng. Chem., 6 (1914), 845) states that the gas must always be run into the oxygen and never in the reverse order, since the higher hydrocarbons are decomposed with the deposition of carbon by the glowing wire.

DISADVANTAGES OF THE ABOVE METHODS USING HEATED PLATINUM WIRE

The original Winkler could be used for rough analyses only since potassium hydroxide or water is used as the absorbing liquid.

In the Dennis Hopkins modification the iron wire which is sealed to the platinum spiral is readily oxidized in the Dennis 'open cup' arrangement.

Bretschger's modification is open to the objection of rather easy breakage at the points of sealing of the platinum wire and difficult repair.

The Scott pipette is expensive because of the long platinum wire; also the wire when heated may sag against the glass, cracking the apparatus.

The submersion of the pipette as applied by Voldere eliminates excessive heating of the pipette but the apparatus is subject to the other errors of the Dennis Winkler pipette.

The chief objections to the Dennis Winkler pipette are: the necessity of having the gas flame at the weakest part of the apparatus-the junction of the capillary and bulb-, the tendency to leakage around the rubber

stopper holding the electrodes, whose arrangement is not entirely satisfactory, and the weight of the mercury on the stopper.

In the Haldane apparatus the compensator in communication with potassium hydroxide bulb would be thrown out of adjustment by the large contraction on combustion of a gas containing a large percentage of methane.

Weaver and Ledig state that their pipette gives satisfactory service and is easily repaired. Assuming this to be the case they eliminate most of the difficulties of the Dennis Winkler pipette.

EXPERIMENTAL

APPARATUS

The various forms of combustion apparatus as described below were connected to a modified Orsat apparatus (Figure 1) built by F. C. Vilbrandt. This consists of a measuring burette (a) provided with a level bulb (b) and compensating device (c); a two way stopcock (d) leading from the common train capillary to allow for the introduction of gases and oxygen; a series of absorption pipettes:- (e) for carbon dioxide absorption, (f) for oxygen absorption (g) for carbon monoxide absorption, (h) a pipette containing water to serve as a reservoir for nitrogen or to remove hydrochloric acid vapors after a carbon monoxide absorption; (m) a stand to hold combustion pipettes. A level bulb (n) provided with rubber tubing and a stopcock (p) serves as a level and as a reservoir for the mercury for the combustion pipette. The stopcock on level bulb (b) aids in regulating the passage of gases to and from the combustion pipette. Air was blown through (k), agitating the water around the burette to facilitate the rapid and even cooling of the gases. (i) was in communication with a cylinder of of liquid oxygen (92% O_2, no hydrogen) and (l) to the gas holder. Stopcock (r) connects the combustion pipettes with the remainder of the apparatus.

Wire gauze was placed around the combustion apparatus to protect the operator from glass particles in case of an explosion during an analysis.

All the absorption pipettes were connected by means of T - tubes (w) and rubber tubing to a water reservoir (v) which acted as a seal to keep air from the absorbing solutions, thus increasing their life and efficiency.

Rubber tubes (t) with glass rods inserted in the ends were substituted for the stopper closing the absorption pipettes. By removal of these rods the pipettes can be emptied and recharged without taking apart the apparatus.

As all parts are supported on the same wooden frame, the entire piece of apparatus can be moved as a unit. However, the rubber connection (x) was necessary because of the strain at this point and consequent danger of breakage.

The measuring burette was calibrated by weighing water forced from the top of the burette by mercury from the level bulb.

In order to avoid the calculation of all observed volumes to volumes under standard conditions the compensating device was attached to the burette. Any given volume of gas in the burette may have its volume under standard conditions read directly by making connection between the burette and compensator and raising or lowering the level bulb until the mercury in the manometer reaches the same level in the two arms of the U tube. Pettersson was the first to show (Zeit. f. anal. Chem., 25(1886),467) that by means of a tube inclosing a volume of gas the error which would result from variations in pressure can be compensated.

A c.c. or so of water acidified with sulfuric acid was placed above the mercury in the measuring burette and all gas readings made from the lowest point on the water meniscus.

The absorption bulbs were provided with glass tubes to increase the surface of the liquid to be exposed and thereby hasten absorption.

The lubricant employed was made according to Dennis (Gas Analysis, 115) from rubber, vaseline and paraffin wax.

COMBUSTION APPARATUS

A. Dennis Winkler pipette with electrode modification.

Bearing in mind the difficulties with this form of pipette as mentioned above (p.32) the same electrode modification as used by F. C. Vilbrandt in a previous Ph. D.° thesis from this laboratory was continued here. This is illustrated in Figure II. The platinum coil is sealed into the glass tubes (a,a) allowing about 3 cm. of it to extend below the seal into the tube. A stout copper or iron wire or rod (b) is provided with a small portion of a No. 00 rubber stopper (c) at the lower end and the rod forced through the stopper. The glass tubes are placed in position through the stopper to be used for closing the lower opening of the pipette. The tubes are inverted, filled with mercury, short rubber tubes (d) slipped over their ends, the rods with the No. 00 stopper are then set into the mercury in the tubes and the rubber tubes on the glass rods slipped over the rubber stopper on the led rods. These are wired into place. When uprighted, a small amoun of air appears at the top of the leads providing an air

space between the mercury and the heated joint when combustion is in progress.

This, as well as the other forms of combustion apparatus used - except D - were made of quartz. This same form of electrode was applied to - B - and - D -, described below.

An improvement whose use was continued in - A -, - B - and - D - is the employment of a section of rubber

FIGURE II.

ELECTRODE MODIFICATION.

tubing long enough to be wired on both the rubber stopper and the bottom of the pipette. This helps support the weight of the mercury and aids in preventing leaks. Note Figure III.

A slight modification in the electrodes was introduced during the last few months. It was often found that mercury would finally leak through the opening caused by forcing a wire through the small rubber stopper (c) used at the bottom of the lead tubes. To avoid this, a short length of platinum wire was sealed into a short glass tube and hooked so as to afford a connection with a copper wire. This was then inserted in the rubber tube (d) in place of the stopper and wire.

B. The Central Upright Burner pipette.

This form of apparatus, as shown in Figure III, is a distinctly new type in that the gas burns in an upright flame similar to that of a Bunsen burner rather than downward as in the Dennis Winkler pipette. It had been devised and experimented within this laboratory, previous to the present investigation, as an attempted improvement upon existing gas analysis apparatus.

The capillary connection (A) is provided with two stopcocks. By opening (B) and closing (C) the oxygen is forced into the pipette. When all but a few cubic centimers of the air has been transferred to the pipette, stopcock (B) is closed and (C) opened so that the air must pass down through (D) and up through (K) into the pipette, thus forcing the mercury out of these tubes. (K) is also made of quartz. If a glass tube is used, it gradually seals up; in addition, as noted in the experimental data, repairs must be frequently made, due to breakage of a glass tube.

When the gas sample is measured and ready to be ignited the stopcock on the level bulb is opened and the current turned on. Stopcock (C) is opened and the inflow of gas adjusted by the stopcock on the measuring burette or stopcock (r) above (A) so that the combustion takes place by a small flame burning at the opening of (K). The platinum coil is placed about one

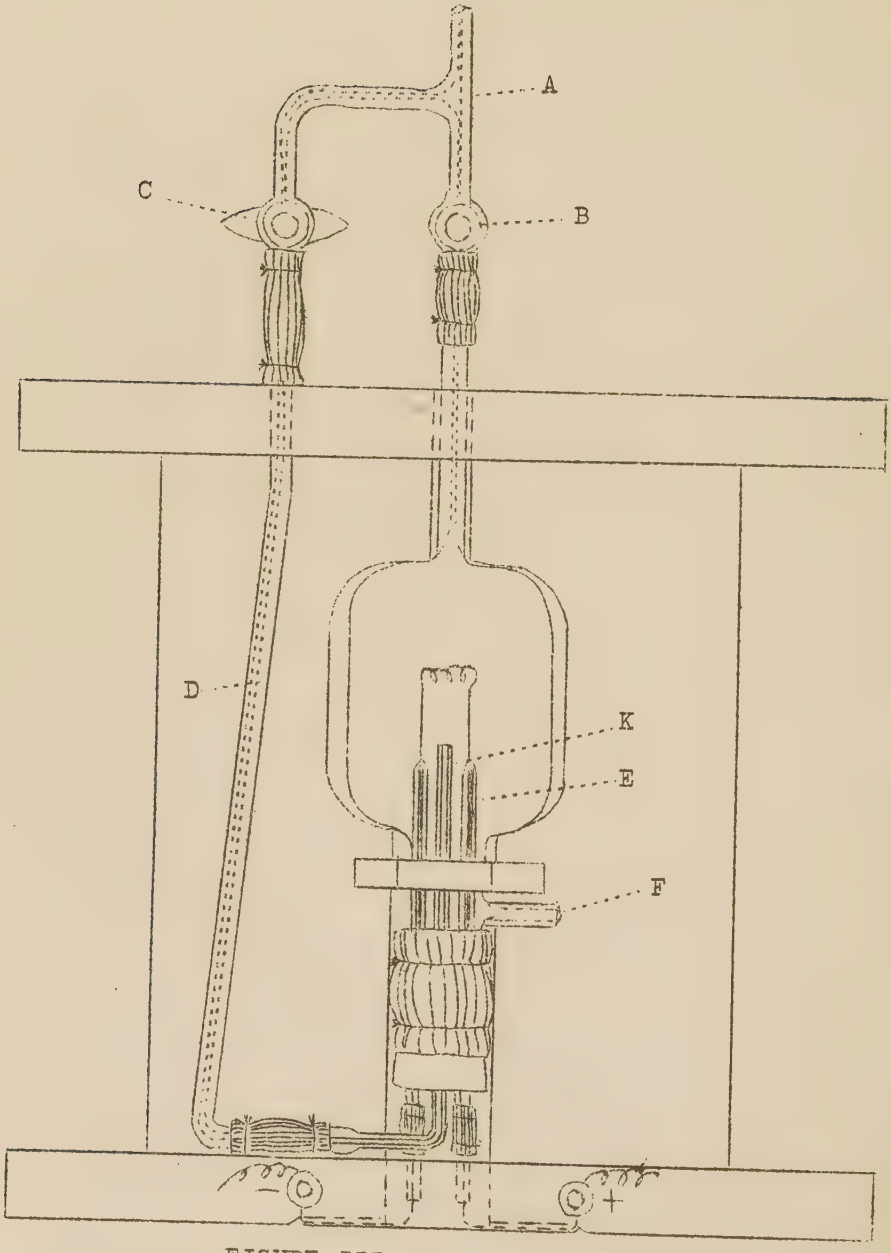


FIGURE III. Central Upright Burner Pipette.

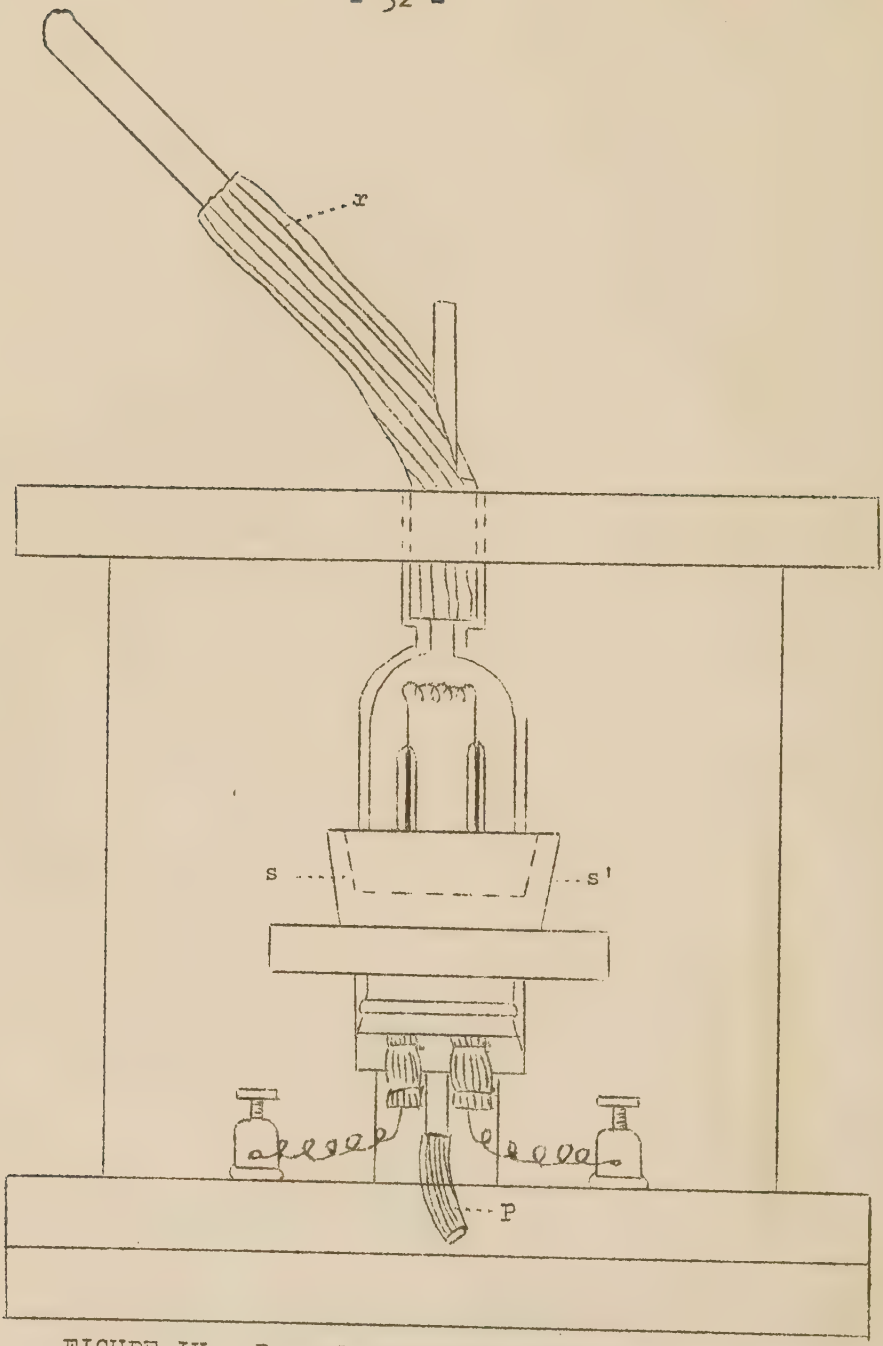
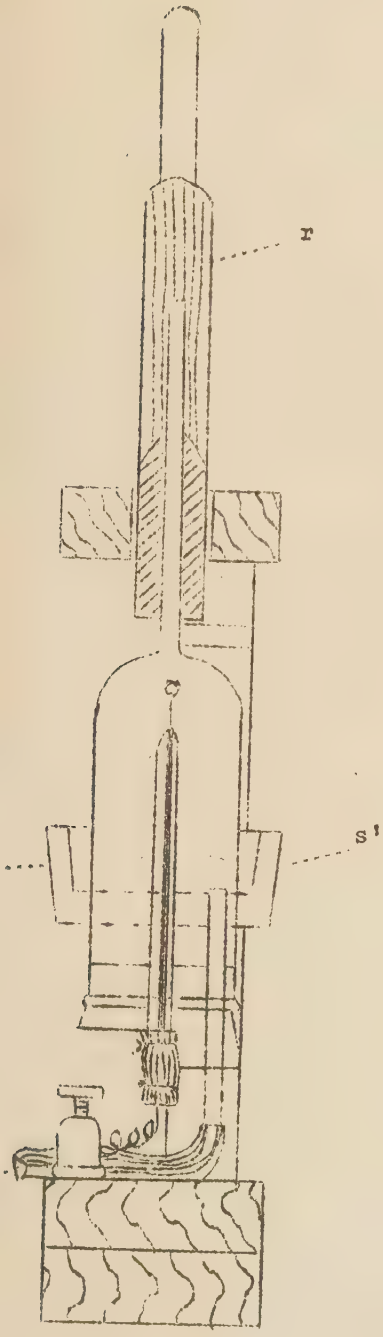


FIGURE IV. Burrel Combustion Pipette (Modified)


r
s'

centimeter above the opening and slightly to one side so as not to be melted by the flame.

C. Burrell Combustion pipette.

The ordinary method of manipulation as given later was followed with the Burrell pipette (which was described on page 30 and in Figure IV) with the exception of the cooling medium. Water flowed over the pipette during combustion and for a short time afterward. (s) is a No. 12 rubber stopper provided with a hole the size of the pipette and a shelving cut out in order toretain water flowing down over the pipette. A hole in the bottom of this stopper is provided with a glass tube and serves as the drain exit for the water.

D. Anderson pipette.

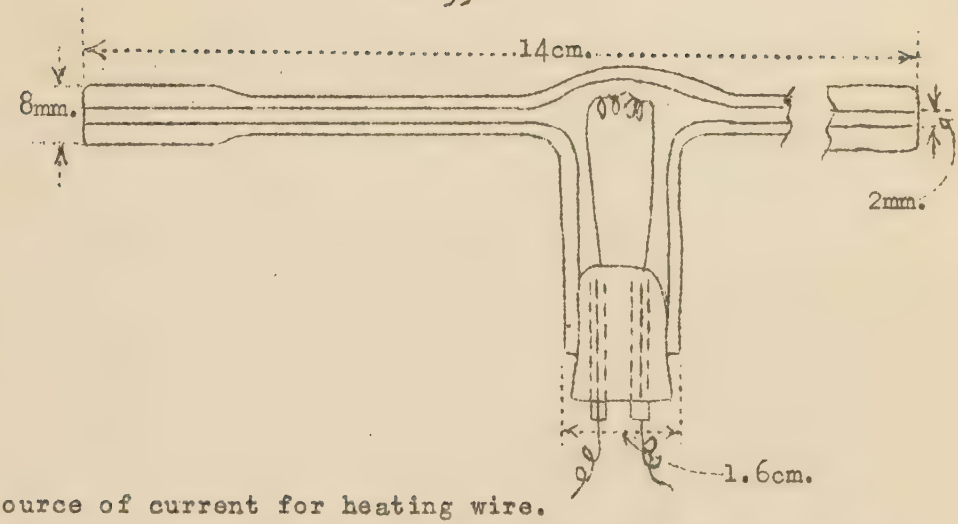
This pipette was obtained too late in the course of the work to permit of any extensive investigation. The pipette is of pyrex and is pear shaped, the small part at the top serving as the entrance for the gas. The bottom is also constricted enough to permit being closed by a stopper as are A and B above. An additional feature of this pipette is the vertical side arm tube placed between the pipette and the level bulb to indicate completeness of combustion. As the gas burns mercury in this side arm falls ceasing to do so when combustion ceases.

E. Capillary combustion pipette.

With the desire to combine the advantages of the Dennis Winkler pipette and of the capillary combustion tube, the apparatus sketched below had been devised in this laboratory, without knowledge of the work of Bleier. This pipette is of quartz. Bleier (Ber., 30 (1897), 697) describes a glass apparatus similar in form but fails to give any dimensions or data regarding its use. (See diagram next page)

Size of pipettes.

A and B have a capacity of about 150 c.c.; C, about 65 cc., and D, a capacity of about 225 cc.



Source of current for heating wire.

An alternating current from the electric lighting circuit was used to heat the platinum wire, being sent through a rheostat whereby the amperage could be regulated. An ammeter was used so that the amperage could be definitely known.

REAGENTS

The mercury used was first distilled, then purified from time to time, by dropping it in a fine stream through sulfuric acid mixed with mercurous sulfate.

The absorbing solutions used; potassium hydroxide, alkaline pyrogallate, and acid cuprous chloride were made according to Dennis, Gas Analysis, pages 225,160 and 232 respectively, and require no description here.

During part of the work sodium pyrogallate solution was used instead of the potassium pyrogallate, according to Jones and Meighan (J. Ind. Eng. Chem., (1919),311) and found satisfactory. The 28% sodium hydroxide solution was found to be most suitable. Jones and Meighan in the above article refer to the work of other investigators upon this substitution.

THE PREPARATION OF METHANE

Methane was prepared as suggested by Burrell and Seibert (Bur. Mines, Bull., 42, p. 46) by the method

of Gladstone and Tribe (J. Chem., Soc., 45 (1884), 154) according to the following equation: $CH_3I + C_2H_5OH + Zn(Cu) = CH_4 + Zn\begin{matrix}I\\C_2H_5O\end{matrix} + (Cu)$.

As suggested by Vilbrandt the method of Walker (J. Chem. Soc., 62 (1892), 717) was followed in the preparation of the methyl iodide.

The gas evolved was purified by passage through a condensing column containing some of the zinc copper couple, to condense the methyl iodide and ethyl alcohol; then through concentrated sulfuric acid and bromine to remove unsaturated hydrocarbons; through sodium hydroxide to remove bromine; over water to catch any sodium hydroxide and finally over copper oxide to remove hydrogen. A bottle of potassium hydroxide solution was added to the train to absorb carbon dioxide frompossible burning of methane as it passed over the copper oxide.

Difficulties encountered.

Based upon the above references no difficulty in generating methane was expected. Trouble was soon met with however. As a rule the copper deposit on mossy zinc tended to be sooty, or quite thin and in either case, not very adhesive. In use this material gave a slow and small gas evolution. Trials with partially renewed materials gave no success. By this time it was concluded that perhaps part of the trouble was due to the method as well as to the manipulation. So further investigation of the literature was made.

Literature.

Criticisms of the method were not numerous but were sufficient to show that the preparation of methane by the method of Gladstone and Tribe has not been altogether satisfactory.

According to Bone and Wheeler (J. Chem. Soc., 81 (1902), 535) the preparation of pure methane by the Gladstone and Tribe method is always a tedious process. If however an aluminium mercury couple be substituted for the zinc copper couple the result is much more satisfactory, the action being more energetic.

Gill and Hung (J. Am. Chem. Soc., 17 (1895), 786) state that the method of Gladstone and Tribe does not yield pure methane owing probably to water in the alcohol used. To obviate this and to prevent possible formation of ethane, they substituted anhydrous methyl alcohol for ordinary alcohol.

However, in regard to this presence of water, Gladstone and Tribe (in the article whence the equation- see page 36 - for the preparation was obtained) give an equation in which water, instead of alcohol is used in the preparation of methane.

Campbell and Parker (J. Chem. Soc., 103(1913),1292) prepare pure methane by the action of water at 90° upon aluminium carbide, better results being obtained than by the Gladstone and Tribe method.

Masiloff and Egloff (J. Phys. Chem. (1918) 570) give the preparation and purification of methane (although they do not refer to this specific method) as one of the problems needing investigation.

Renshaw and Greenlaw (J. Am. Chem. Soc., 42 (1920), 1472) in an article upon the preparation of zinc methyl state that apparently the greatest difficulty in the preparation of zinc alkyl compounds is in obtaining a highly active zinc copper couple. A number of investigators have made recommendations for its preparation but in the judgment of the writers, as the matters stand, the accomplishment is an art rather than a science. In general the experienced worker will at first find difficulty in preparing couples as active as those described by Lachmann and by Gladstone and Tribe.

They carried out a number of experiments under various heat treatments using commercial zinc dust with finely divided precipitated copper. Couples were obtained which were fairly active with ethyl iodide, but none of them were as active as the products prepared later from 30 mesh zinc and precipitated copper, nor were they nearly as active as the couples prepared from zinc filings by Gladstone and Tribe. In the absence of a catalyst they were all acted upon very slowly by methyl iodide. At least a partial explanation of the greater

activity of the granulated zinc couples is believed to lie in greater porosity which allows a better penetration of the iodide.

For the preparation of a suitable zinc copper couple they recommend to mix nine parts of zinc powder passing a 30 mesh sieve with one part of copper precipitated from solution by zinc and to heat the mixture gradually in a combustion tube, the tube being rotated rapidly, until the zinc turns first a yellow color and then forms into little pellets of a tarnished lead color. The heating is then stopped, the couple cooled in hydrogen and used. Methyl acetate is used as a catalyst for the preparation of zinc methyl, 1 c.c. being added to 110 gms. of methyl iodide before it is run on the zinc copper couple. The mixture is left overnight and then heated at 60° the next day, condensation being complete in about seven hours.

Modification of the Gladstone and Tribe method.

The use of granulated zinc instead of mossy zinc had been considered and it was decided to make some trials with its use. It was quickly found that more copper could be deposited upon a given volume of zinc, that the deposit was in much better physical condition and that the methane was evolved with much greater rapidity. However, the evolution ceased comparatively soon so that the volume of gas obtained was rather small. This was partly due to the fact that considerable methyl iodide decomposed, iodine being deposited in the sulfuric acid and in the first bromine bottle. A mixture of the granulated and mossy zinc was an improvement, eliminated part of the above disadvantages and the adherence of some of the granulated zinc to the mossy variety, aided in producing a better deposit of copper upon the latter. There still remained some uncertainty as to results, the method "happening' apparently, to work better at some times that at others.

However, the last sample of gas was prepared from a mixture of the two varieties of zinc containing a little more than half granulated zinc by weight. The methane was of as good a quality as any previous sample, no iodine was deposited and 15-16 liters were made in about 8 hours.

Removal of hydrogen from the gas.

In the purification of the second holder of the gas which was prepared, it was hoped to remove the hydrogen, However, the glass tubing at hand seemed of very poor quality and after breaking several tubes and admitting air to the gas, it was decided to use the gas without further attempts at purification. In the next preparation, better tubing was available but 2 - 3 per cent hydrogen remained even after passing the gas over reoxidized copper oxide several times. For methods of comparison with the gas previously used, it was decided to make no further attempts at purification of the gas, about the same percentage of hydrogen being present in both cases.

The fact that the gas when analyzed showed a small but consistent percentage of hydrogen may have its significance in view of the discussion in the introduction.

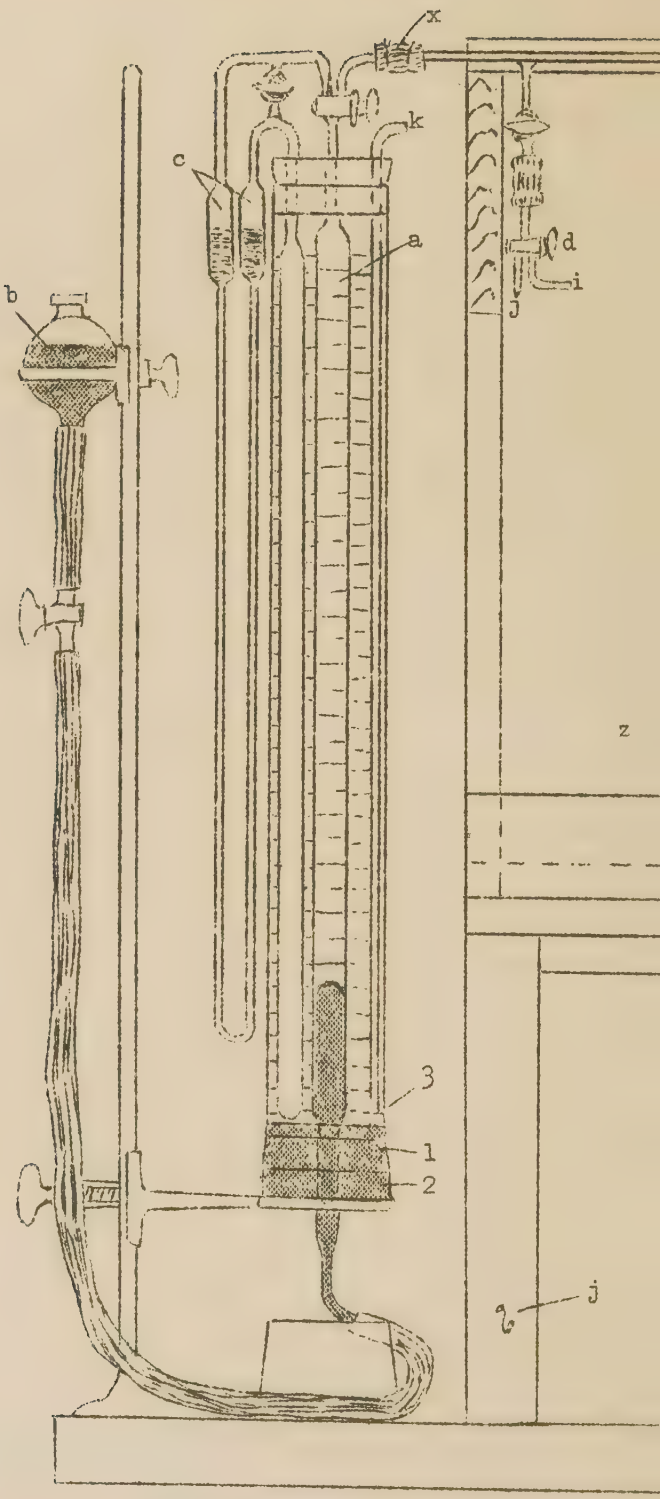
ABSORPTION LOSS OF METHANE

On testing a holder of gas for carbon monoxide-after absorption in potassium hydroxide and alkaline pyrogallate-a slow but continual loss in volume was noted. This was not due to manipulation of leaks for nitrogen (from the air) subjected to the same treatment did not diminish in volume. Similar losses were obtained by treatment with fuming ($18\%SO_3$) sulfuric acid.

A loss of 3.5 cc. in 67.1 cc. sample was observed after six days during which time probably 90-100 passages back and forth were made and 39 readings taken, the gas standing over the solution the remainder of the time. Another test showed a loss of 1.7 cc. in a 67 cc. sample in 42 hours. After this test the gas was subjected to absorption in pyrogallate solution with no ensuing decrease in volume.

65.4 cc. gas decreased to 63.6 cc. in 5 hours when passed several times with shaking, into fuming sulfuric acid and then into potassium hydroxide.

On investigation of the literature in this regard most text books on gas analysis state that there is no known absorbent for methane.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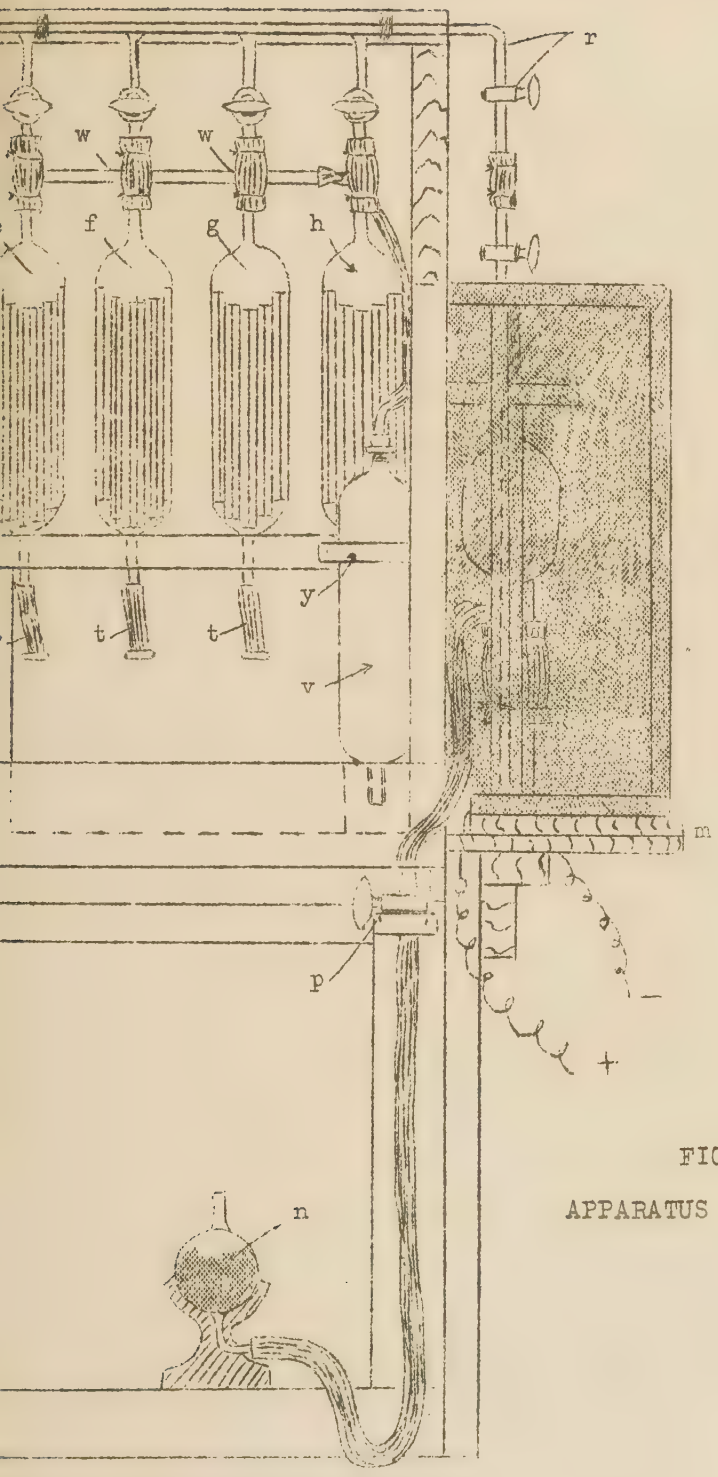


FIGURE I.

APPARATUS ASSEMBLED

Literature.

Hempel (Ber., 20 (1887), 2341) states that cuprous chloride absorbs ethylene.

Lewes (J. Soc. Chem. Ind., (1891), 407) states that with ordinary coal gas, cuprous chloride absorbs unsaturated hydrocarbons. He also states it to be well known that in using sulfuric acid, one did not absorb any of the paraffins and that methane is absorbed in only alcohol, paraffin and in olive oil. Ethylene is absorbed in cuprous chloride but ethane is not.

Worstall (J. Am. Chem. Soc., 21 (1899), 245) found daily absorption of methane from methyl iodid e or natural gas in fuming sulfuric acid. For the first there was a 45.4 per cent loss in 11 days and a total loss of 71.7 per cent after this was sealed over fuming sulfuric acid for 3 months. From natural gas there was a daily absorption of 1.4 per cent. After 25 per cent methane from natural gas was absorbed, the remainder showed less than 0.1 per cent absorption per hour.

Anderson (J. Ind° Eng. Chem., 6(1907), 989) obtained a decrease of about 2 cc. after 30 passages of nearly pure methane into fuming sulfuric acid ($30\%SO_3$).

Burrel and Seibert (Bur. of Mines, Bull., 42, 46) report absorption of methane by both fuming sulfuric acid and cuprous chloride but not of methane.

Czako (J. Gasbel., 57 (1914), 169) finds that in accord with some results by Ab-der-Halden (J. des Usines a Gas, 19(1913), 296) methane is appreciably soluble in aqueous reagents, including cuprous chloride, used in gas analysis. The error is negligible if the determinations are carried out properly, using the smallest possible quantity of reagents and avoidance of shaking.

Considering Czako's work, however, the question arises, as to just when all of the carbon monoxide is absorbed and when methane absorption begins.

Demorest (Met. Analysis, Lord and Demorest, 1916 Ed., 288) states that upon prolonged contact fuming sulfuric acid or bromine will absorb some methane and ethane.

This however, is negligible if the time of contact is not prolonged beyond five or ten minutes.

Discussion.

The loss in this case may be due to methane or to some other gas as ethylene or ethane but the loss is small and would affect the results but slightly. Since the gas was to be used as a means of comparison of different dorms of apparatus, it was deemed inadvisable and unnecessary to spend further time on this question.

However, this absorption and supporting evidence from the literature throws doubt on the accuracy of precise gas analysis of unsaturated hydrocarbons and of carbon monoxide by the ordinary methods in the presence of methane and of methane itself if part of it may be absorbed before combustion. Considering all three possibilities a total error of one percent might be rather easily involved.

SLOW COMBUSTION PROCEDURE

The following general procedure was followed in making an analysis. The oxygen was measured first, passed into the pipette, and then the gas measured and passed into the oxygen so as to come into contact with the hot platinum coil. After the first passage which was slow enough to allow the gas to burn with a very small flame, three additional passages of 15 or 20 cc. were made back into the burette so as to allow the gas in the capillaries to burn. No appreciable differences in results were obtained by small variations in the rapidity of the gas passage. On the average the platinum coil (24 gauge, 0.02 inch) was red, a $7\frac{1}{2}$ - 8 ampere current being used, for at least two minutes.

With the capillary combustion pipette, the gases were mixed by being passed back and forth three times or a total of six passages. Four such passages were employed in burning the gas. Additional passages were tried in both cases at times without appreciable differences in results. When explosive mixtures were used the gas was moved just fast enough to prevent a series of small explosions. Variations were tried here also

but the total time for a capillary combustion was ordinarily four minutes.

During combustion and for a short time afterward the combustion pipettes were cooled by a current of air.

After combustion the residual gas was measured and passed into potassium hydroxide to absorb the carbon dioxide. Carbon dioxide remaining in the capillaries was removed by sending the gas into the combustion pipette and back into the potassium hydroxide several times.

That volume was taken as final from which there was no decrease after two or more successive absorptions.

According to Burrell, Anderson, Dennis and others, the molecular volumes of different gases vary slightly from the theoretical values, carbon dioxide notably and corrections must be made therefore in accurate gas analysis.

The corrections used were based upon the work of Anderson (J. Ind. Eng. Chem., 11 (1919), 299). However, his corrections apply to natural gas, so that n, the average number of carbon atoms per hydrocarbon molecule, is more than one instead of less than one as is the case with the methane used. Also Anderson has a much higher percentage of carbon dioxide in the gases after combustion. So for these reasons it was necessary to plot curves based on figures given in the article referred to and extend the lines to fit our case. The assumption is made that corrections obtained by such figures are of value. (See tables and curves following)

The natural gas contains no hydrogen whereas the methane used in these combustions contains about 3 - 4 per cent. Based upon Wohl's work (Ber., 37, (1904), 429) a correction for the molecular volume of hydrogen is necessary. As explained below, however, such a correction was not applied.

The following figures were obtained from Landolt and Bornstein, (1912 Ed., p. 150) for hydrogen:

Mol. wt.	specific gravity theoretical	specific gravity observed	observer	theoretical / observed
2.016	0.06965	0.0696	Rayleigh	1.0007

One liter of oxygen weighs 1.2988 gm. at 45° at sea level. According to Morley one liter of hydrogen weighs 0.089875 gm. as compared to 0.0900 obtained by previous investigators and 0.06952 is its specific gravity. Using these values which are accepted as accurate, the molecular volume for hydrogen would be one. Again, (Bull. 42, 85) gases need not have their molecular volumes corrected if their pressure is considerably below one atmosphere. In this methane the partial pressure of the hydrogen is very low, being around 15 mm. This value is obtained in the following manner:

$$2/3\ (\text{total contraction} - 2\ CO_2) = \text{cc. hydrogen}$$

$$\frac{\text{cc. of hydrogen} \times 760}{\text{gas volume after combustion}} = \text{mm. partial pressure}$$

For the above reasons no corrections are deemed necessary for the hydrogen. In most cases these corrections applied below changed the value of the methane and hydrogen but 0.1 - 0.3 per cent.

The following form was used in recording and computing the results.

	As read	Corrected (from burette calibration)	
cc. gas	23.50	23.12	
cc. oxygen	94.75	95.18	
Total		118.30	
after combustion	74.40	74.75	
total contraction (T.C.)		43.55	
volume after KOH (after CO_2 absorption)	53.20	53.60	
cc. CO_2		21.15	
$\%CO_2$ (in gas after combustion)		28.0	
n		0.9621	from $\frac{3\ CO_2}{2T.C.-CO_2}$
c, correction factor for n		1.0011	from chart

	As read	Corrected (From burette calibration)
nc	0.9631	
c', correction factor for V	0.9989	from chart
V, hydrocarbon volume,	21.96	from $\frac{CO_2 \times 5c'}{n}$
P,% hydrocarbons	94.98	from $\frac{100\ V}{cc.\ gas}$
CH_4, % methane	91.47	from P x nc
H_2, % hydrogen	3.50	from $P(1-n^c)$

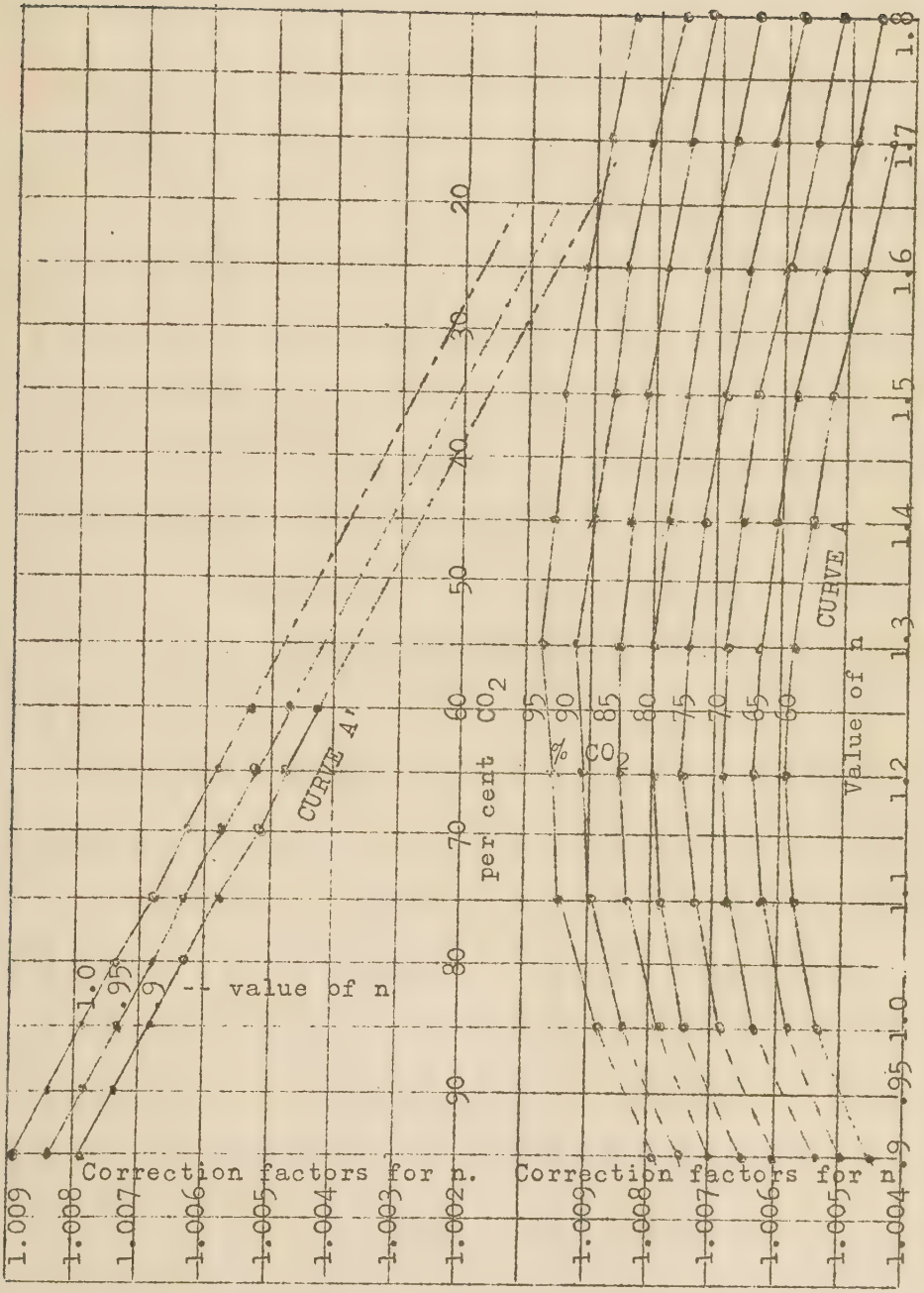
The method of obtaining the correction factors used in this work is as follows:

Curves A and B were plotted from Tables II and III in the article by Anderson (J. Ind. Eng. Chem., (1919), 299) - curves A and B. These curves were then extended so that new correction factors could be obtained (the per cent CO_2 being 60 - 95 per cent inclusive and n being 0.9 - 1.0 inclusive). On applying these values and again extending curves (A') and(B'), additional correction factors are obtained for lower percentages of carbon dioxide (20-60 per cent CO_2) n being 0.9 - 1.0.

The values obtained in this manner by extrapolation are listed in the following Table.

TABLE OF CORRECTION FACTORS

	FOR n			FOR HYDROCARBON VOLUMES		
	value of n					
$\%CO_2$	0.9	0.95	1.0	0.9	0.95	1.0
20	1.0003	1.0007	1.0012	0.9994	0.9992	0.9990
25	1.0009	1.0012	1.0017	0.9991	0.9989	0.9987
30	1.0014	1.0018	1.0022	0.9988	0.9986	0.9984
35	1.0019	1.0023	1.0028	0.9987	0.9985	0.9983
40	1.0024	1.0028	1.0033	0.9983	0.9981	0.9979
45	1.0030	1.0034	1.0038	0.9980	0.9978	0.9976
50	1.0035	1.0039	1.0043	0.9977	0.9975	0.9973
55	1.0040	1.0044	1.0048	0.9974	0.9972	0.9970
60	1.0045	1.0049		0.9971	0.9969	
65	1.0050	1.0054		0.9968	0.9966	
70	1.0054	1.0059		0.9966	0.9964	
75	1.0060	1.0065		0.9963	0.9961	
80	1.0065	1.0070		0.9960	0.9958	
85	1.0070	1.0075		0.9957	0.9955	
90	1.0074	1.0079		0.9955	0.9953	
95	1.0079	1.0084		0.9952	0.9950	


Correction factors for n.
1.009
1.008
1.007
1.006
1.005
1.004
1.003
1.002
1.0
.95
.9 -- value of n
CURVE A
per cent CO_2
20
30
40
50
60
70
80
90
95
% CO_2
85
80
75
70
65
60
CURVE A
Value of n
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
Correction factors for n.
1.009
1.008
1.007
1.006
1.005
1.004
.9
.95
1.0

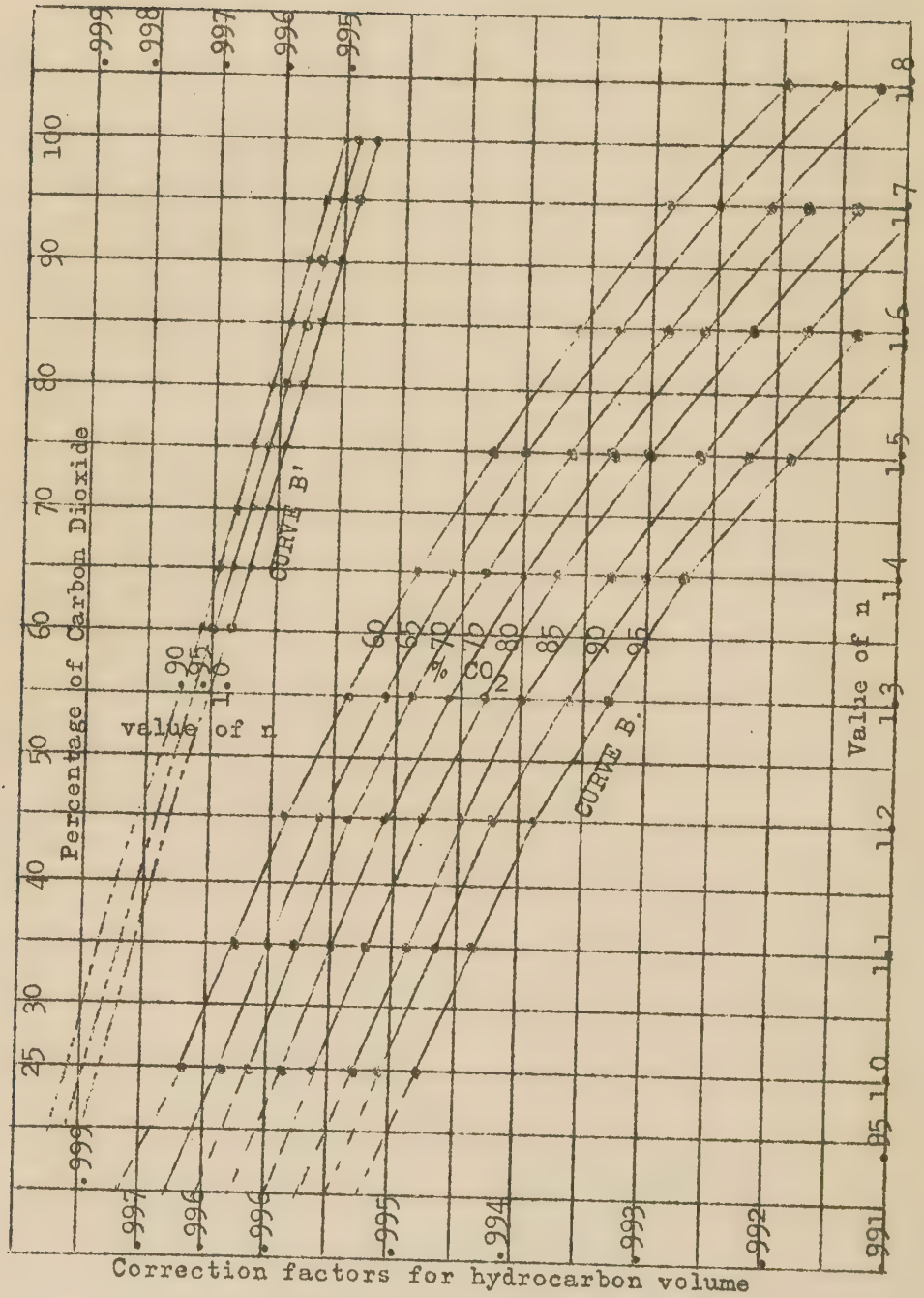

Correction factors for hydrocarbon volume
Percentage of Carbon Dioxide
Value of n
CURVE B'
CURVE B
% CO2
.999
.998
.997
.996
.995
.994
.993
.992
.991
.990
.995
.996
.997
.998
.999
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.85
1.90
1.95
25
30
40
50
60
70
80
90
100
60
65
70
75
80
85
90
95

TABLE I. GAS I.
Dennis Winkler pipette

Run	cc. oxygen	cc. gas	% CH_4	% H_2	Sum
		Oct. 21.			
1	85.00	27.35	87.98	2.19	90.17
2	89.07	30.07	85.80	2.59	88.39
3	85.20	29.27	83.68	5.20	88.89
4	75.17	25.02	87.59	2.86	90.45
5	88.37	26.64	88.84	0.20	89.04
6	84.21	26.34	85.95	3.72	89.67
7	84.81	26.64	87.23	2.90	90.13
8	85.50	26.23	86.27	2.83	89.10
	Ave		86.36	3.18	89.54
		Oct. 22.			
9	89.17	27.85	90.69	8.20	98.89
10	91.17	26.03	83.45	5.56	89.01
11	87.18	23.51	85.07	3.45	88.52
12	85.20	26.33	84.28	4.93	89.21
13	89.37	24.34	83.80	7.20	91.00
	Ave		84.15	5.28	89.43
		Oct. 26.			
14	91.62	23.71	88.99	8.60	97.59
15	86.99	21.20	85.45	1.44	86.89
16	87.88	22.31	85.62	3.31	88.93
17	88.92	22.21	85.86	2.33	88.19
18	87.78	21.00	86.03	2.07	88.10
19	88.67	20.80	86.19	4.00	90.19
	Ave		85.83	2.63	88.46
		Oct. 27			
20	83.22	21.75	86.12	2.34	88.46
21	87.38	25.33	85.42	3.37	88.79
22	87.98	24.03	86.20	2.80	89.00
23	87.68	20.70	85.59	3.83	89.42
	Ave.		85.83	3.09	88.92

Oct. 28

Run	cc. oxygen	cc. gas	% CH_4	% H_2	Sum
24	90.97	22.11	86.17	2.06	88.24
25	92.20	20.65	85.58	5.22	90.80
26	92.28	21.75	85.83	3.46	89.29
27	87.78	19.00	85.70	2.04	87.74
28	94.82	21.70	85.68	2.70	88.38
	Ave		85.79	3.10	88.89

Nov. 3

49	94.42	21.70	85.27	3.34	88.61
50	94.63	19.60	85.55	3.27	88.82
51	92.59	19.00	85.34	2.54	87.88
	Ave		85.39	3.05	88.44

Central Upright Burner pipette.

Oct. 29

29	90.17	22.61	83.82	4.50	88.32
30	91.78	19.40	83.69	1.56	85.25
31	93.30	20.00	83.49	15.50	98.99
32	94.42	22.21	83.75	4.81	88.56
33	94.62	19.90	84.19	9.74	93.93
34	94.93	20.60	83.87	7.88	91.75
35	95.28	21.25	84.32	4.53	88.85
	Ave		83.90	3.85	87.75

Nov. 2

36	93.50	20.80	84.18	4.67	88.85
37	93.10	19.05	83.72	3.73	87.45
38	96.34	23.71	83.15	6.52	89.67
39	95.43	21.80	84.06	4.07	88.13
40	94.61	19.75	83.54	3.65	87.19
	Ave		83.88	4.03	87.91

Nov. 3

41	96.75	21.55	83.79	7.58	91.37
42	97.26	23.84	83.42	4.97	88.39
43	98.26	21.30	83.49	4.63	88.12
44	98.58	21.05	84.73	7.00	91.73
45	95.73	20.85	84.60	3.60	88.20

Nov. 3, cont.

Run	cc. oxygen	cc. gas	% CH_4	% H_2	Sum
46	93.60	20.62	82.89	5.83	88.12
47	96.24	23.40	82.33	5.66	87.99
48	94.60	21.10	83.78	4.41	88.19
	Ave		83.63	5.39	89.02
Average of runs, Table 1					
Winkler pipette			85.67	3.34	89.01
Upright Burner pipette			83.76	4.66	88.42

Note. Runs underscored are what might be termed 'irregular' runs and are not included in the averages. An explanation of them is included in the discussion.

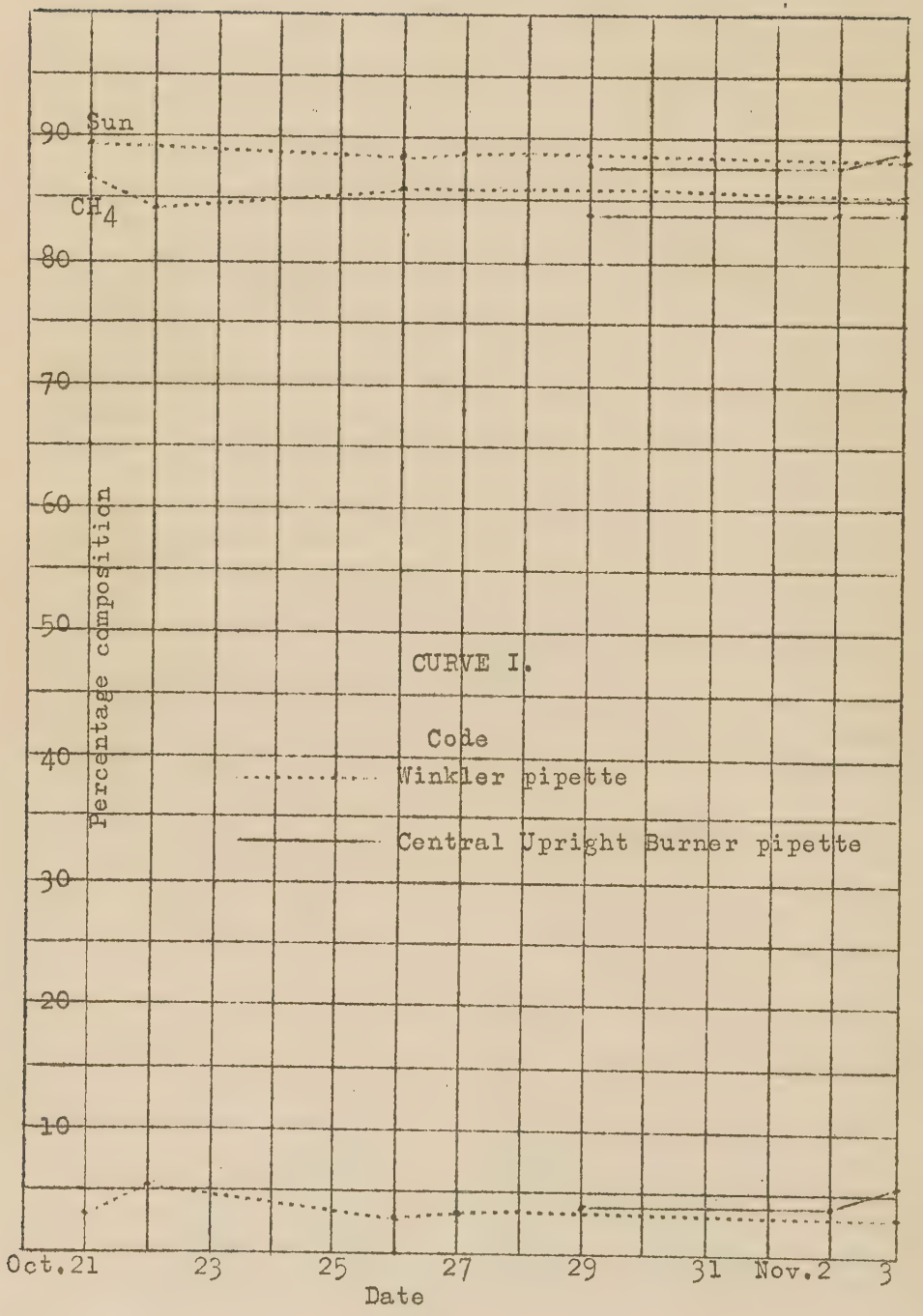
DISCUSSION

On examination of the above set of figures and curves it is quite evident that the percentage analysis of the gas differs with the pipette used.

With the Central Upright Burner pipette a higher percentage hydrogen but a lower percentage methane and a lower percentage of total combustibles is obtained. All these runs were made on the same sample of gas. A further discussion of this point is reserved until after a second table of values. Similarly, explanation is postponed for the gradual decrease in the percentage of combustible gases, from the beginning to the end of the table.

Practically all analyses accompanied by accident, interruption or faulty or irregular manipulation are omitted. Some of these appear to be accompanied by definite analytical differences and few such runs are added by way of illustration. These are underscored not being included in the average of the day's analyses.

#'s 9,14 and 34 are "first runs". After cleaning the pipette or part of the apparatus, the first analysis made usually differed from the average of the rest in the series, the difference consisting, generally, in a higher percentage of hydrogen. A series of runs with this point in view was begun but interrupted by some


Sun
CH_4
90
80
70
60
50
40
30
20
10
Percentage composition
CURVE I.
Code
Winkler pipette
Central Upright Burner pipette
Oct. 21
23
25
27
29
31
Nov. 2
3
Date

other phase of the problem and the three of four analyses thus made were not consistent enough to form the basis for a conclusion.

At times a slight explosion would occur after a volume of the gas entered the pipette. As might be expected, this occurs readily if the Central Upright Burner pipette is improperly operated so that the first cc. or so of the gas may be sent into the pipette from the top (because the top is the customary place of entrance of the gas in combustion pipettes) rather than through the entrance tube. Here again the results were high in hydrogen. Note 31, 33, 38.

On the other hand flashing (backfiring in the capillary or entrance tube) caused a low percentage hydrogen as in 5 and 30. At times, in the Dennis Winkler pipette, the mixture of gas and oxygen on the second passage over the coil happened to be such that a flash as distinguished from an explosion resulted. In the Central Burner type such conditions were encountered at times when a large side tube rather than a capillary was used as noted in the next table, or if, water was present in the entrance tube, to obstruct the continuous passage of the gas.

It should be remarked here that, while the percentage hydrogen has been discussed above, according to the hypothesis stated in the introduction, hydrogen may not actually be present. The contraction (giving hydrogen, according to customary gas analysis calculations) may be due to oxidation products, as methyl alcohol, formaldehyde and formic acid.

The low percentage methane and low percentage hydrogen obtained on Oct. 22, is unexplained. According to the notes a large flame was used in these runs and may have affected the results.

TABLE II. GAS II.
Winkler pipette

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
			Dec. 13		
52	23.12	95.18	91.47	3.50	94.97
53	21.99	92.98	89.34	4.88	94.22
54	22.96	94.42	91.27	2.24	93.51
55	24.32	96.45	91.78	2.79	94.57
56	20.80	95.98	91.51	2.92	94.43
57	22.20	95.03	92.61	1.31	93.92
58	20.80	94.52	91.73	2.17	93.90
59	20.20	92.49	91.86	2.64	94.50
60	20.61	91.59	92.94	1.38	94.32
	Ave.		91.90	2.37	94.26
			Dec. 14		
61.	21.25	97.06	92.02	4.45	96.47
62	22.21	93.65	91.67	2.57	94.24
63	22.01	92.95	91.59	2.50	94.09
64	23.22	93.20	91.78	4.43	96.21
65	25.21	93.50	91.14	3.43	94.57
	Ave		91.55	3.23	94.78
			Jan. 5		
95	22.30	96.25	91.05	2.71	93.76
96	22.80	97.71	91.69	1.86	93.55
97	23'46	98'11	88'94	4'45	93'39
98	26.44	98.98	90.56	3.84	94.40
	Ave		91.10	2.80	93.90
			Jan. 6		
99	24.97	95.53	90.69	3.26	93.95
100	24.22	100.33	88.90	7.47	96.37
101	22.82	99.40	91.73	2.27	94.00
102	21.20	95.69	90.58	3.29	93.87
103	22.71	96.85	89.39	5.06	94.45
104	22.49	94.93	90.13	3.16	93.29
	Ave		90.50	3.40	93.90

Jan. 8

Run	cc. gas	cc. oxygen	% CH_2	% H_2	Sum
105	24.01	97.97	90.52	3.94	94.46
106	22.71	96.55	90.92	3.75	94.67
107	21.36	94.52	91.19	3.51	94.71
	Ave.		90.88	3.73	94.61

Jan. 10

108	21.91	94.50	91.25	1.90	93.15
109	23.84	94.47	90.92	2.12	93.04
110	23.25	91.96	92.18	3.35	95.53
111	23.63	93.84	92.03	2.04	94.07
112	22.71	91.27	88.28	5.77	94.05
	Ave.		90.62	2.96	93.58

Upright Burner pipette

Dec. 15

66	24.82	96.60	88.94	6.11	95.05
67	23.21	93.91	88.75	5.00	93.75
68	21.68	95.81	90.06	3.07	93.13
69	22.61	94.43	89.60	6.33	95.93
70	24.82	94.52	89.52	4.31	93.83
71	25.33	97.46	92.19	3.11	95.30
72	21.81	95.94	90.98	3.49	94.47
73	22.80	96.84	89.74	3.56	94.30
	Ave.		89.97	4.37	94.34

Dec. 17

74	25.48	98.38	91.38	3.79	95.17
75	19.95	94.33	91.81	2.51	94.32
76	22.16	92.54	89.93	4.98	94.92
77	25.43	99.19	91.63	2.91	94.54
	Ave.		91.61	3.07	94.68

Dec. 30

78	22.91	98.48	86.73	5.82	92.54
79	23.01	99.13	84.27	7.82	92.09
80	25.02	97.56	88.85	4.75	93.60
81	24.22	99.29	87.70	4.62	92.32

Jan. 3

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
82	23.21	95.48	88.27	4.16	92.46
83	22.91	96.09	90.12	2.72	92.84
84	22.00	96.00	89.11	4.75	93.86
	Ave.		89.17	3.88	93.05
		Jan. 4			
85	21.40	95.13	90.63	1.61	92.24
86	22.39	92.70	89.15	3.26	92.41
87	25.05	95.03	89.53	4.32	93.85
88	25.63	93.83	90.05	3.32	93.37
89	23.21	95.23	90.12	3.33	93.45
90	22.71	95.48	89.29	3.22	92.51
91	22.46	94.92	90.05	2.96	93.01
92	23.85	94.94	89.61	3.81	93.42
93	21.55	94.22	91.32	2.51	93.83
94	24.57	94.12	89.49	4.40	93.89
	Ave.		89.92	3.28	93.20
	Average of runs, Table II				
	Winkler pipette		91.19	2.98	94.17
	Upright Burner pipette		89.83	3.78	93.61

Notes.

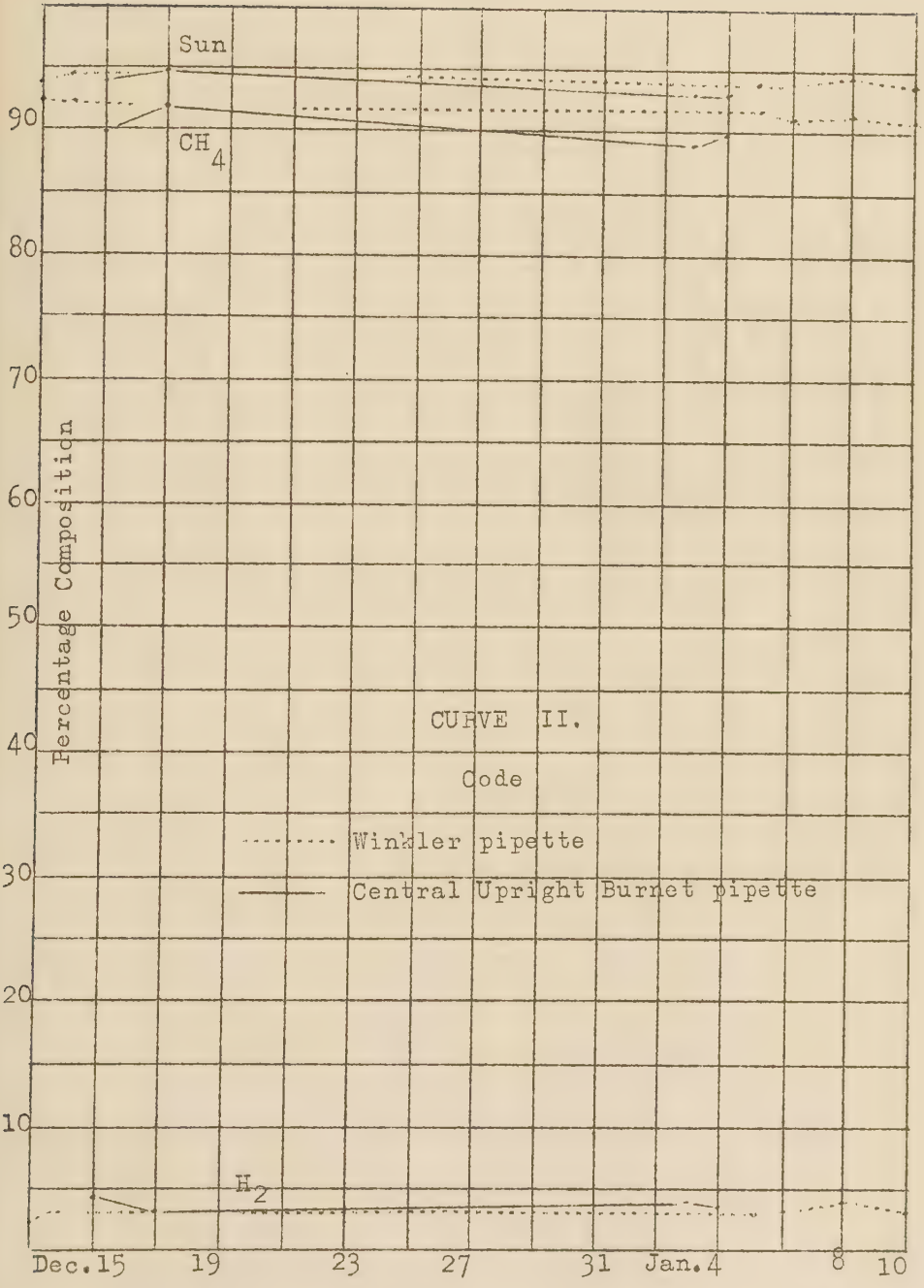
#'s 53, 61 and 100 are noted as 'first runs'.

A slight explosion occured in #'97 and 110.

These two points have been discussed at length under Table A.

DISCUSSION

Runs 66-73 inclusive, were somewhat irregular in combustion being accompanied by flashing and slight 'popping' in the entrance tube. The percentage hydrogen is a little higher in these cases than the average obtained in later analyses. It will be noticed in Table I that explosions cause a higher percentage hydrogen while flashing was accompanied by a lower percentage hydrogen. Flashing and popping together, seem to average these extremes. As the capillary side tube first used had been


Sun
CH4
H2
90
80
70
60
50
40
30
20
10
Percentage Composition
Dec. 15
19
23
27
31
Jan. 4
8
10
CURVE II.
Code
Winkler pipette
Central Upright Burnet pipette

broken and a tube (not capillary) substituted in its place, it was thought that the trouble might lie here. This was evidently a correct conclusion for much more regular runs were obtained after a capillary side tube had been inserted.

As mentioned in the procedure for analysis, the pipettes were cooled during the combustion and for a short time after ward by a current of air. As a matter of curiosity, a number of runs were made during which the pipettes were not cooled. This would be rather reckless with glass pipettes but the quartz pipettes were not injured by the heat. Presence or absence of cooling did not affect the results as obtained with the Winkler pipette but with the Upright Central Burner pipette, appreciably higher methane percentages were obtained. No cooling was used in runs 83, 88 and 93 nor in 74, 75 or 77 (compare with 76). A few preliminary runs not recorded here could be offered as additional evidence.

As proof of the necessity for proper coil position in the Central Upright Burner pipette, runs 78 - 81 are inserted. Here the coil was placed about one half inch above the entrance tube instead of about one fourth inch. The results obtained did not check very well among themselves and were low. The further the coil is placed from the entrance tube (or from the capillary in the case of the Dennis Winkler pipette) the more nearly is an explosion pipette made of the combustion pipette. It has been previously remarked that the explosion of a small part of the gas sample results in high hydrogen. It would be interesting at this point to analyze the gas by the explosion method (that is, subject the entire sample of the gas to explosion) to see if the results in this case would again be high in hydrogen.

It was found impractical to use a glass entrance tube instead of a quartz entrance tube (at least with the glass tubing available) as but a few runs could be made before the top of the tube would be broken off or melted together. The apparatus is sufficiently inconvenient as regards repairs without adding to the difficulties.

Based upon runs 74, 75, 76, and 77 in which a glass entrance tube of small opening-about 1 mm. in diameter- was used, similar quartz tubes were ordered to be used in further investigation of the effect noted. As mentioned above cooling was used only in 75. Although these three runs (even though agreeing satisfactorily) fornish insufficient data for a general conclusion, the percentage methane is much higher than obtained in any other trials with this type burner and is equal to that obtained in the Dennis Winkler pipette. A possible disadvantage is the splashing of mercury in a small stream from such a tube on the pipette with resulting oxidation.

It is also reasonable to suppose that the use of a tube with a small opening would produce more complete combustion, for a slower passage of gas is necessitated and possible-without backfire into the tube- and a larger flame is produced.

Neglecting these few runs, however, the advantages and disadvantages of the Central Upright Burner pipette as compared with the Dennis Winkler may be summed up as follows:

1. The Central Upright Burner pipette eliminates excessive heating at the junction of the capillary with the pipette proper. However, this is no advantage when quartzware is used- as the quartz Dennis Winkler inuse in this laboratory for several years shows no signs of deterioration-.

2. More attention is required in its use because of the additional stopcock and the necessity of driving the mercury down the side tube and up the entrance tube (which to avoid mercury oxidation, should be done before the current is turned through the coil) else the error due to that volume must be neglected. On the other hand, the operator can see the flame, as the gas is burning and thus regulate the entrance of the gas. Perhaps this is a matter of personal manipulation as no difficulty was experienced in adjusting the rate of gas passage into the Winkler pipette, even though the flame was not readily seen.

3. The set up of the pipette is more inconvenient due to the additional side entrance tube.

EXPLANATION OF DIFFERENCE IN ANALYTICAL RESULTS

- Dennis Winkler vs. Upright Burner pipette -

The only suggestion or explanation advanced as to the lower percentage of methane resulting from the use of the latter type pipette, is that based upon runs 74, 75, 76 and 77.

That is, in the regular analytical procedure, possibly the flame is so small that some gas passes through without combustion. It is possible to have a larger flame but this necessitates a smaller opening or a faster rate of gas passage into the pipette, but the latter plan increases the chance for incomplete combustion.

TABLE III GAS II
Burrell pipette

Jan. 11

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
113	14.15	44.89	87.10	5.83	92.93
114	12.33	46.48	87.43	4.22	91.65
115	11.48	45.90	89.03	3.57	92.60
116	14.29	47.96	90.30	2.42	92.72
117	12.17	45.39	87.40	4.22	91.62
	Ave.		88.25	4.05	92.30

Jan. 12

118	13.89	46.18	89.26	3.32	92.58
119	13.79	49.22	89.57	3.03	92.60
120	12.79	43.57	89.00	3.57	92.57
121	11.87	45.90	89.03	3.05	92.08
122	14.10	44.48	88.56	2.36	90.92
123	11.78	48.85	89.59	2.38	91.97
124	13.90	48.24	89.26	2.33	91.59
125	11.57	47.20	89.20	3.52	92.74
	Ave.		89.19	2.94	92.13

Jan. 19.

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
139	12.28	44.19	88.60	1.55	90.15
140	12.94	48.61	89.12	2.30	91.42
141	12.76	46.91	88.42	3.27	91.69
142	12.41	47.11	88.59	2.79	91.38
	Ave.		88.68	2.48	91.16

Winkler pipette

Jan. 12

126	21.35	94.98	90.53	2.72	93.25
127	24.02	94.72	92.06	1.32	93.38
128	20.60	90.20	89.67	5.76	95.43
	Ave.		90.75	3.27	94.02

Jan. 15

129	19.20	93.00	89.04	4.65	93.69
130	21.00	96.55	89.62	3.95	93.57
131	22.36	97.26	89.96	3.73	93.69
	Ave.		89.54	4.11	93.65

Jan. 19

145	22.71	96.26	90.48	1.02	91.50
146	18.60	96.24	89.16	4.98	94.14
147	22.02	93.02	90.41	2.10	92.51
	Ave.		90.02	2.70	92.72

Burrell (with Upright Burner) pipette.

Jan. 17

135	13.39	48.41	87.08	5.31	92.39
136	12.08	46.60	88.05	3.26	91.31
137	12.43	44.88	87.07	4.56	91.63
	Ave.		87.40	4.39	91.78

Jan. 19

143	12.99	47.26	89.27	4.03	93.30
144	12.54	48.93	88.35	5.11	93.46
	Ave.		88.81	4.57	93.38

Burrell pipette-note below.

Jan. 15

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
132	11.46	47.21	84.78	8.33	93.11
133	11.48	47.16	85.96	7.42	93.38
134	12.46	46.40	88.15	3.58	91.73
	Ave.		86.30	6.44	92.74
Average of runs in Table III					
Winkler pipette			90.10	3.36	93.46
Burrell pipette			88.79	3.15	91.94
Burrell pipette fitted with Upright Burner			87.96	4.46	92.42

Notes.

Runs 132, 133 and 134 were made with the Burrell pipette but with the coil removed farther than customary from the capillary opening.

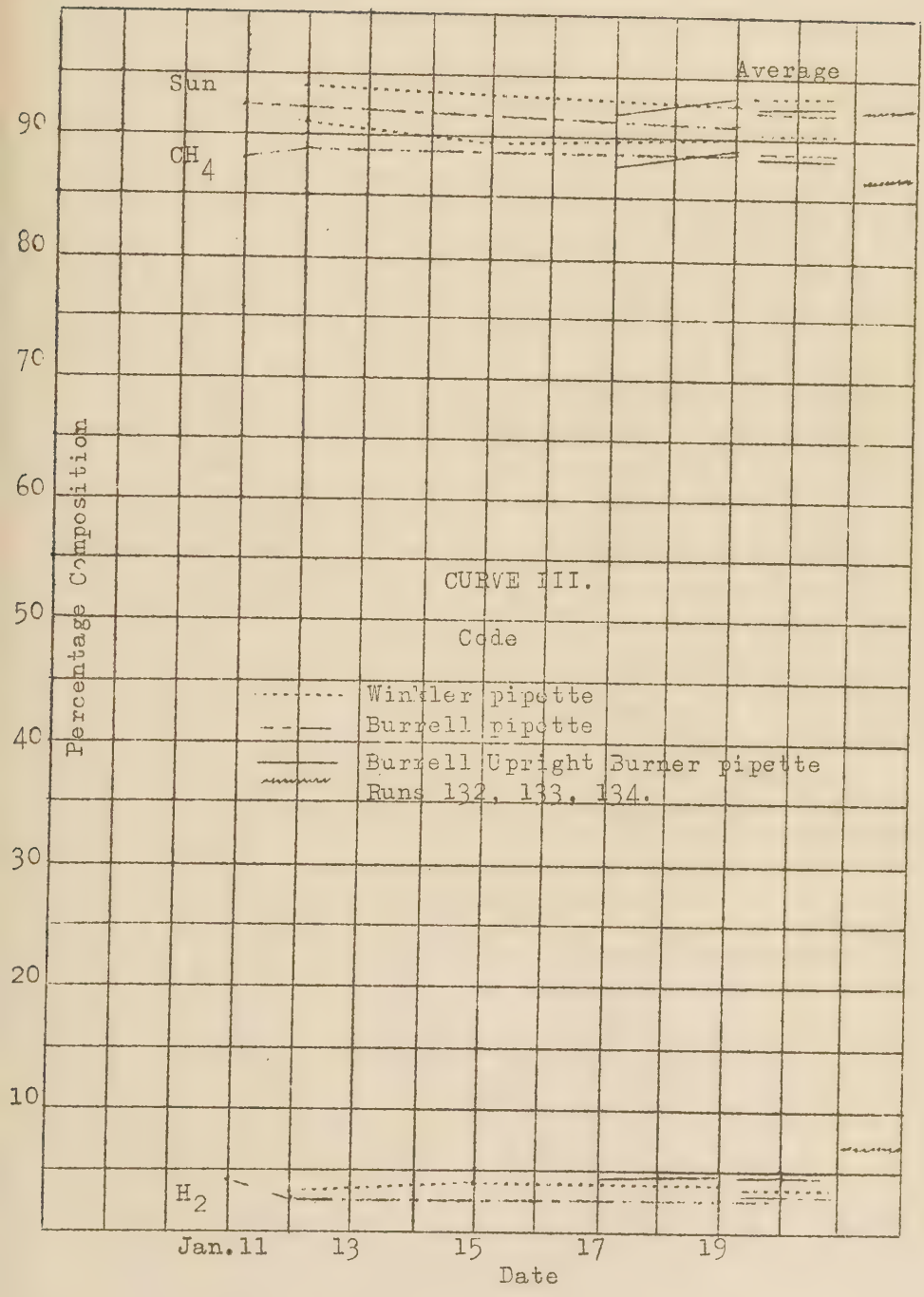
Water cooling was used on the Burrell pipettes.

In runs 143 and 144, the opening of the entrance tube (glass) was very small.

No preliminary or practice runs were made on the Burrell type but the combustion seemed to proceed regularly and satisfactorily. More practice in manipulation of this type pipette might change the results.

Discussion.

The results in Table III merely confirm those of the previous Tables hence repeated discussion is omitted. The only addition is in regard to a comparison of the Dennis Winkler and Burrell pipettes. The Burrell pipette has a smaller capacity and hence a smaller sample of gas must be used. This would be expected to cause greater variation in results but not necessarily a lower average. Possibly the cause for a lower percentage methane is inherent to the pipette (shape or size) but no experimental observations assist in the explanation.


Average
Sun
CH_4
H_2
90
80
70
60
50
40
30
20
10
Percentage Composition
CURVE III.
Code
Winkler pipette
Burrell pipette
Burrell Upright Burner pipette
Runs 132, 133, 134.
Jan. 11
13
15
17
19
Date

OBSERVATIONS ON THE CAPILLARY COMBUSTION PIPETTE.

As described under the various forms of apparatus this pipette consists, essentially of a platinum coil in a capillary enlargement.

Various difficulties were encountered in setting up the capillary pipette and a large number of runs were made previous to the ones given above.

Following the method of Bleier (Ber., 1897,697) the pipette was closed by a rubber stopper through which platinum wires were inserted. To avoid the probability of breakage of the glass'lead in' tubes (due to the small size of the pipette and accompanying high heat) Khotinsky cement and water glass were used - but without success - to fill the openings in the rubber stopper. Glass tubes were then used but the platinum wire from the coil was passed through the tubes, sealed outside the pipette, a hook being formed for connection to the current. The other end of the tube, projecting into the pipette, was almost sealed and the tubes filled or almost so with mercury. Later, when plaster of Paris was used as a covering for the stopper, the same material closed these tubes and the arrangement was found to be quite satisfactory.

The combustions in the first runs were accompanied by a large number of small explosions and flashes which were prevented by placing platinum wires in the capillaries on each side of the combustion chamber. These wires tended to clog the mercury and to hold any possible dirt so were later removed and after further experience with the apparatus, found to be unnecessary to prevent explosions.

Volatilization of the stopper resulted in combustion, causing a very dirty pipette. This volatilization continued after a number of combustions had been made, the same stopper having been in continuous use. Plaster of Paris was tried as a substitute for the stopper but without great success, especial difficulty being met in removal in case of breakage or necessary cleaning of the pipette. A layer of mercury covered with acidulated

water prevented volatilization of the stopper but was otherwise unsatisfactory for mercury gradually crept into the pipette and raised the water level so that the water came into contact with the platinum wires causing electrolysis and gas evolution.

By this time it was decided that satisfactory service would not be obtained with the pipette in the vertical position, for the mercury creeps along the capillary and falls into the pipette causing a change in the volume of the system as well as oxide formation. Inversion of the pipette does not remedy matters for the apparatus is slightly curved and mercury collects in the depression near the coil. After these trials the chamber of the pipette was placed and used in a horizontal position.

As a covering for the stopper to prevent volatilization Khotinsky cement and various Bakelite enamels were found unsuitable due to melting. A water glass covering served very well but being alkaline is open to the objection that it absorbs carbon dioxide.

A layer of plaster of Paris, about one fourth of an inch thick prevents volatilization and is easily applied. In addition to cooling by a blast of air it was found advantageous to wrap a small cloth around the stopper and part of the pipette and to keep this moist during the combustion.

It will be noted that in the runs of Table IV, the mixtures are within the explosive limits. Earlier runs were characterized by numerous explosions and flashes. It was found after a number of runs that by increasing the speed with which the gas passed over the coil, that these pops could be eliminated. In the future therefore, the gas movement was made just fast enough to avoid these little explosions. There still remained an explosion occuring when the platinum coil became red hot. The force of this explosion was greatly lessened by a rather rapid gas movement just as the coil was about to become red hot but this procedure is somewhat awkward and inconvenient.

This large volume of gas was used merely to approximate the volumes used in the other pipettes. A few runs were made later in which non explosive mixtures were used.

TABLE IV GAS II.
Capillary pipette

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
			March 5		
148	17.60	91.68	79.61	3.85	83.46
149	15.80	93.81	85.57	1.84	87.41
150	16.10	94.62	87.70	2.54	90.24
151	15.65	95.23	90.02	0.65	90.67
			March 7		
152	13.09	94.11	79.19	17.52	96.71
153	15.30	93.10	82.39	11.92	94.31
154	16.70	94.01	78.29	21.17	99.46
155	18.90	93.81	78.22	11.62	89.84
156	18.50	92.90	85.94	4.76	90.70
			March 8		
157	18.60	92.88	84.66	5.18	89.84
158	13.19	85.60	84.79	3.30	88.09
159	18.25	91.47	84.21	5.00	89.21
160	17.50	91.17	83.79	3.48	87.27
161	16.40	92.03	83.12	9.02	92.14
			March 9		
162	17.60	95.53	80.94	7.18	88.12
163	15.38	91.08	83.92	3.92	87.84
164	19.50	94.67	85.90	4.00	89.90
165	19.80	93.40	85.36	3.93	89.29
166	18.38	96.04	85.96	7.55	93.51
167	20.82	95.73	87.45	3.86	91.31
168	17.30	94.82	88.48	1.81	90.29
			March 10		
169	18.20	97.36	77.85	18.58	96.43
170	21.30	94.60	83.80	11.60	95.40
171	19.00	94.60	88.53	0.36	88.89

Jan. 11

Run	cc. gas	cc. oxygen	% CH_4	% H_2	Sum
172	20.60	96.55	87.79	5.66	93.45
173	17.80	92.08	89.32	3.26	92.58
174	20.10	96.65	88.19	1.26	89.45
175	19.40	91.57	85.22	1.53	86.75
		Jan. 12			
176	18.40	94.31	82.41	4.27	86.68
177	21.10	94.01	80.50	4.10	84.60
178	19.80	95.18	87.55	1.74	89.29
179	18.60	94.11	88.06	0.97	89.03
180	17.00	90.80	70.33	9.32	79.65
181	17.60	93.10	75.97	6.79	82.76
182	19.30	94.82	82.49	3.83	86.32
183	16.29	94.22	88.45	0.87	89.32
184	17.20	93.40	74.54	8.25	82.79
	Ave.		83.68	5.85	89.53

Notes.

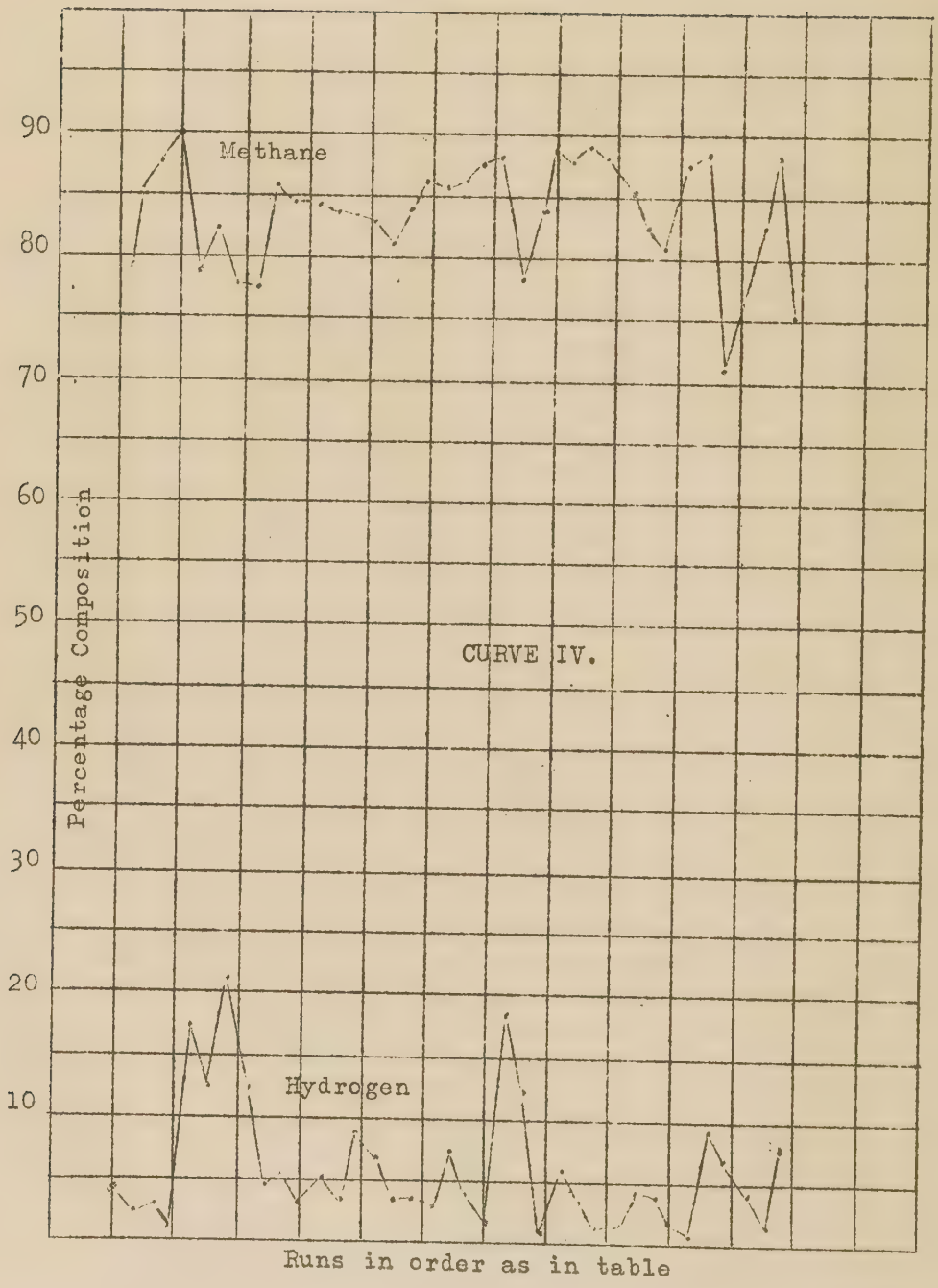
On March 8th, the pipette was filled with mercury after the combustion, no gas remaining in the capillary pipette itself.

On the other runs, after combustion the mercury was drawn in as far as the pipette chamber leaving the latter full of gas. Carbon dioxide was absorbed from the gas in the capillary while that in the pipette itself was calculated, the volume of the pipette having been found.

Several runs were made to compare the carbon dioxide in the pipette as found by calculation with that obtained by washing the contents of the pipette into potassium hydroxide and absorbing the carbon dioxide. Results were the same and the absorption method was employed from that time, it being more convenient.

Three analyses made, Mar. 16, on the Winkler pipette averaged:

CH_4	85.16 %
H_2	3.56 %
Sum	88.72 %


90
80
70
60
50
40
30
20
10
Methane
Hydrogen
Percentage Composition
CURVE IV.
Runs in order as in table

DISCUSSION

Conditions and manipulations were practically the same during all these runs, as far as could be told, hence these large variations are not easily explainable. Changing the position of the coil varied the results. The practical impossibility of completely avoiding an explosion on ignition of the coil and the great difficulty and care in diminishing its force are sources of variation.

Some of the runs might be thought to compare favorably with the average value obtained on the Winkler but the three analyses averaged in the above percentage were carried out when the holder was almost empty, the last previously recorded analyses with the Winkler showing several per cent more methane.

The chief disadvantages of the capillary pipette as compared with the Winkler pipette are:

1. More time is required in an analysis.
2. It is necessary to pass the gas back and forth several times in mixing and burning.
3. Additional time is required in combustion.
4. It is sensitive to slight changes, such as a change in the position of the coil.

A great advantage is the fact that it is easy to take apart and set up for necessary cleaning and repairs.

THE CAPILLARY PIPETTE WITH NON-EXPLOSIVE MIXTURES

According to Parker (J. Chem. Soc., 105(1914)1002) about 6 per cent methane in oxygen and methane mixtures forms the minimum explosive mixture. With the gas in use it was found possible to mix 7.5 cc. gas with 75 cc. oxygen (or a 10 per cent mixture) and burn this in a capillary pipette without danger of explosion. Such a procedure removes the difficulty occurring in the preceding analyses but is subject to the errors inherent in the use of a small sample, that is, any error in reading is multiplied many times in the final percentage composition.

Unsatisfactory results were obtained from a number of runs using 7 - 10 per cent methane, other conditions of manipulation being the same as used heretofore. Gas of 89 per cent methane content (by the Dennis Winkler pipette) analyzed 69 - 74 per cent by the above method. Some otherwise apparently satisfactory runs, varied considerably from these figures.

SUGGESTION FOR USING THE CAPILLARY PIPETTE

Hence in using this pipette it is recommended that a mixture containing 20% or more methane be used in the combustion and that care be taken to avoid an explosion or to lessen it as much as possible. Too violent an explosion resulted in nothing more than some little loss of time due to the blowing out of the stopper.

INCOMPLETE COMBUSTION IN THE CAPILLARY PIPETTE

Naturally such low results (69 - 74 per cent methane) as given above aroused curiosity as to the cause.

So the apparatus was arranged to make it possible to send the gas mixture after such a combustion into the Winkler pipette. To do this little additional apparatus was necessary other than a three way stopcock between the burette and the two types of combustion apparatus which were placed side by side.

Regular manipulation with the capillary type gave 83 per cent methane which was increased to 90 per cent after passage into and combustion in, the Dennis Winkler pipette. A similar mixture (one containing 9 per cent gas) required four successive combustions in the capillary pipette before no forther contraction was observed. That is, after the first run, the carbon dioxide was absorbed and the mixture passed over the hot coil several times and carbon dioxide again absorbed, etc. until there was no further contraction. After this, combustion in the other pipette gave an additional one per cent methane, no contraction being observed after the first trial. The final percentage methane was 89.98 per cent, as compared to 75.00 per cent after the first run.

The next step was to try a similar method of procedure with the Dennis Winkler pipette and a similar condition was found here. Several runs were carried out and failed to give complete combustion when the gas was analyzed as usual, it being necessary to use two or three successive combustions before a constant value was obtained. That is, it seemed necessary to absorb the carbon dioxide formed before further combustion would occur. No experiments were made to determine the effect of long time exposure of the gas to the hot wire although the fact that a higher temperature of the coil (9 - 10 amperes) failed to give complete combustion of the gas in the ordinary time of analysis seems toaid the contention expressed in the previous sentence.

CAUSE OF INCOMPLETE COMBUSTION

This incomplete combustion might reasonably be due to the formation of incompletely oxidized products, such as methyl alcohol, or formaldehyde or to an insufficiently hot coil whereby all the methane was not burned during the first passage.

OBSERVATIONS ON METHYL ALCOHOL, FORMALDEHYDE, ETC., FORMATION.

To test for formaldehyde, alkaline phloroglucinol was used. This is prepared by adding 25 per cent sodium hydroxide solution to an equal volume of approximately 1 per cent freshly prepared phloroglucinol ($C_6H_3(OH)_3$). A solution (40%) of formaldehyde when diluted to contain one part formaldehyde in one hundred thousand (1 in 100,000) of water solution produced a perceptible red coloration when added to the phloroglucinol reagent. Hence, it is evident that formaldehyde sufficient to affect the analytical results as mentioned previously, or as discussed in the introduction, will be readily detected by this reagent.

To test the gaseous products of combustion they were bubbled at a very slow rate through several cc. of water and a portion of this tested for formaldehyde by addition to the reagent. Into the other portion of this solution was thrust a red hot copper spiral several

times (to oxidize any possible methyl alcohol) and the test for formaldehyde applied.

No formaldehyde reactions appeared in anumber of single runs.

Water through which the gas from two combustions of a 10 per cent mixture of methane and oxygen was passed, contained no formaldehyde or methyl alcohol.

Similarly the cumulative effect of four runs, two as above and two with a 25 per cent methane mixture, produced no formaldehyde color reaction.

Although a very faint rose color was observed after the preceding solution had stood half an hour or so, traces of pure formaldehyde gave a distinct reddish coloration, rather than a rose color.

Similar experiments with a Winkler pipette (the above being with the capillary pipette) failed to give a test for formaldehyde, or methyl alcohol.

A distinct red coloration was observed but once in a test. The water, amounting to about one cc., from several analyses with the Anderson pipette, when poured into the alkaline phloroglucinol produced a red coloration. This however was but transient and corresponded to not more than one part formaldehyde in several thousand of solution.

No conclusive information can be given at present in regard to the formation of formic acid under similar conditions in amounts exceeding traces. This is due to the fact that no very sensitive tests have been found as yet from the literature or by experiment which will apply to the small amount of material available for testing.

COIL TEMPERATURE AND COMPLETENESS OF COMBUSTION

With regard to the coil temperature, although the few analyses given were made rather hastily yet they certainly indicate a more complete combustion with higher amperage and resultant higher temperature of the platinum coil. Thus, with the capillary pipette:

	7.8 amp. (red coil)	9 amp. (yellow white coil)
% CH_4	86.61	88.03 (A)
% CH_4	78.07	88.14 (B)

(B) was made after changing the position of the coil, so that conditions were slightly different than in (A).

With the Winkler pipette:

	7.8 amp.	8.5 amp.	9.5 amp.	10.5 amp.
% CH_4	86.43 86.77	87.69	88.51	88.50

In these tests on incomplete combustion it was noticed that while the percentage methane increased with successive combustions of the sample, that of the hydrogen remained the same or decreased. Assuming the incomplete combustion to be caused by a low coil temperature, such percentage comparisons might be expected for the fractional combustion of methane and hydrogen over copper oxide depends upon the burning of the hydrogen at a lower temperature. The opposite takes place under certain conditions, however, as noted by Bancroft(Trans. Am. Electrochem., Soc., 32 (1917), 465; J. Phys. Chem. 21 (1917), 644) in an article which contains references to work on fractional combustion.

Literature.

It was known that different investigators used different platinum coil temperatures but as far as remembered there had been recorded no extensive investigation of the relation of completeness of combustion to coil temperature. Hence, during some of the above observations, the following somewhat contradictory information was found fromthe literature.

Reichenberg (Chem. News, 73 (1887), 158) uses a combustion tube in which a platinum wire is brought to redness.

Thorner (Chem. Zentr., (1890) I, 136) also passes the gas back and forth several times (an explosion burette is used) before full combustion of the methane is accomplished.

Hankus (Chem. Zentr., (1899), I, 803) passes the gas slowly back and forth four times over a spiral for combustion, after which all the methane is burned.

Grehant (Chem. Ztg., (1907), 1109) obtains complete combustion of a mixture of methane and air by

passing it over a red hot platinum coil, only after several hundred passages.

Hempel (Zeit. angew. Chem., (1912), 1841) states that it is difficult to obtain complete combustion of gases in the Dennis modification and that some of the gas escapes detection.

Burrell and Seibert (Bull. 42, p. 19, 40) employ a white hot platinum wire kept at this heat for two minutes.

Dennis (Gas Analysis, 153) brings the platinum spiral to a red heat and keeps it at this heat for sixty seconds after the gases have been introduced into the pipette. Tests were made as to the formation of oxides of nitrogen and while increase of temperature of the spiral increased the formation of the oxides, the amount was not measurable in a Hempel burette over mercury, even after heating the air for five minutes with the spiral at a bright yellow heat.

White (Gas and Fuel Analysis, 56) states that a flame combustion as inthe Dennis Winkler pipette is not accurate and that a temperature high enough for complete oxidation causes formation of oxides of nitrogen.

Demorest (Met. Analysis, Lord and Demorest, 282) uses a platinum wire heated to a dull yellow. If heated hotter than to a dull yellow, he declares that there is a slight error due to formation of N_2O_4; if less, combustion is apt to be incomplete.

Winter (Brennstoff Chem., (1920), 17) reports complete combustion of a mixture of pure methane and air containing 5-9.2 per cent methane and imcomplete combustion, in a mixture containing 9.2 - 14 per cent methane.

Ott (J. Gasbel., 63 (1920), 219) gives a table of results in which methane was passed 23 times over red hot platinum in a quartz capillary before a constant volume was reached. 15 passages sufficed to give within 0.05 cc. of the value. Another case is given (a shorter quartz tube being used) in which 50 passages were required, 25 passages bringing the volume to within 0.05 cc. of the final volume.

PERCENTAGE DECREASE OF METHANE

On looking over the analyses and curves it will be noticed that there is a gradual lessening in the percentage of methane. Thus, using the same apparatus, the same holder of gas analyzed 91.90 % methane on December 13, and 90.62 per cent methane on January 10.

This may be due to a very slow leak in the holder, or to a faster rate of solution of methane in the water in the holder, methane being more soluble in water than oxygen, hydrogen or nitrogen, or, to both. At any rate the oxygen content increased as shown by the following analyses of two different samples of gas:

	% O_2	% O_2
At the beginning	1.33	1.60
One week later	1.80	2.00
Three weeks later	2.28	2.50
Four weeks later		2.50

ANDERSON PIPETTE

This pipette was obtained at the close of the work so that there was no opportunity to subject it to an extensive investigation. As previously described it is a pear shaped apparatus provided with the gas entrance at the top of thepipette and with a side arm as an indicator of complete combustion.

EXPERIMENTAL

One run was made with this pipette to see if complete combustion is really indicated by this side arm apparatus.

When mercury ceased to fall in the tube the gas analyzed 88.28 per cent methane and 4.30 per cent hydrogen. After no further loss by carbon dioxide absorption could be obtained, the analysis was 89.84 per cent methane and 4.10 per cent hydrogen. If other runs would check this observation-that there is combustion after it is complete according to the indicator-the obvious suggestion would be the trial of a capillary tube rather than the 6-7 mm. tube sent with the apparatus.

A number of runs were made comparing the Dennis Winkler pipette and the Anderson pipette. In the first two series of runs, the same time was used for combustion. Three runs were then made in which a longer time was allowed for combustion, that is, the gas was passed in more slowly. An 8 ampere current was used in all cases.

Dennis Winkler pipette

% CH_4	86.07	87.75	87.28	87.19	87.02
% H_2	5.30	3.20	3.46	4.71	3.17
Sum	91.37	90.95	90.74	91.90	90.19

Anderson Pipette

% CH_4	85.25	86.11	86.01	85.98
% H_2	4.35	2.82	3.59	3.93
Sum	89.60	88.93	89.60	89.91

Later runs

% CH_4	87.22	86.93	87.67
% H_2	4.18	2.72	3.89
Sum	91.40	89.65	91.56

Discussion

The 86.07 per cent methane in the first Dennis Winkler result was another 'first run'.

According to the above results the same speed of the first passage of the gas over the platinum coil results in more complete combustion in the case of the Winkler pipette. But owing to the shape of the Anderson pipette a comparatively large flame is produced as the gas burns. So a slower gas passage can be used, giving a much more visible flame than in the Winkler pipette and the same percentage results. In regard to this flame visivility the Anderson has a decided advantage but it has a greater capacity than would seem necessary, the disadvantage being that a considerable weight of mercury is required and also a stron support for the pipette.

CONCLUSIONS

1. Quartz combustion apparatus gives very satisfactory use, hundreds of analyses having been made on the forms herein described, without breakage or any kind of deterioration.

2. The possibility of absorption of methane in acid cuprous chloride and fuming sulfuric acid was confirmed. The loss of methane, although slight, is enought to lessen the accuracy of determination of methane, carbon monoxide, and unsaturated hydrocarbons. Most textbooks state that there is no known absorbent for methane but a few references were found mentioning the above possibility.

3. Sodium pyrogallate, recommended by various experimenters as an absorbent for oxygen in gas analysis, instead of potassium pyrogallate, was found satisfactory in this work.

4. An improvement in the method of preparation of methane by the method of Gladstone and Tribe was introduced. The literature first examined in regard to this method indicated it as being rathersatisfactory. In practice, however, and as noted by a few experimenters, this was not the case. A mixture of granulated and mossy zinc, instead of mossy zinc alone, was found to give better though not entirely satisfactory results.

5. The modification of electrodes as used by Vilbrandt in the combustion pipettes was found satisfactory and another slight modification introduced.

6. Work was continued on the Central Upright Burner pipette devised and experimented with in this laboratory before the beginning of this thesis. This type might have an advantage over combustion apparatus made of glass, because of the fact that it eliminates heating at the junction of the capillary and the pipette itself. Compared with a Dennis Winkler pipette made of quartz, the latter is easier of manipulation and gives results about 1.5 per cent higher in methane. Several runs made with a glass entrance tube of smaller opening (one half to one millimeter) resulted in a percentage of methane as high as had been obtained in a Dennis Winkler pipette. Quartz tubes of this smaller opening had been ordered but did not arrive in time to test this point further.

7. A new form of quartz capillary pipette was experimented with. A number of runs were made before it was adapted and prepared for use. As compared with the pipettes previously used, it has a great advantage in the ease with which it may be prepared, cleaned and put into service. Under actual working conditions, it proved unsatisfactory, small changes in the position of the coil and unknown factors seeming to make decided changes in percentage results.

8. The products of the combustion of methane as carried out in gas analysis were tested for formaldehyde and methyl alcohol. Indications were that these might be present but to an extent not exceeding mere traces. The same is true of formic acid although the evidence is not so conclusive as no method of testing for formic acid was found which was as sensitive as that for formaldehyde.

9. A few experiments indicated the desirability of having some standard method of procedure for the combustion of gas in analysis. It was found that several successive combustions were necessary before complete combustion could be attained and that a higher coil temperature tended to give more complete combustion, the latter being of course, well known.

10. An Anderson pipette arrived too late for an extensive investigation but the little experimental work done with it would indicate it to be a satisfactory piece of apparatus. However, it is suggested that the glass tube used as an indicator for complete combustion be replaced by a capillary tube as the former is not sensitive enough for the purpose.

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AUTOBIOGRAPHY

I, Charles Ferdinand Rudmann, was born in Ironton, Ohio, January 19, 1894. I received my secondary school education in the parochial and public schools of Ironton; my undergraduate education from the Ohio State University from which I obtained the Degree of Bachelor of Arts in 1915. During the year 1915-1916 I assisted in the Freshman Chemistry Department receiving the Degree of Master of Arts in 1916. From 1916-1918, I was chemist with the Kentucky Solvay Coke Company, Ashland, Kentucky; from 1918-1919 I was in the Chemical Warfare Service in Washington, D.C. During the summer of 1920 I was in the operating department of the Koppers By Product plant of the Toledo Furnace Company, Toledo, Ohio. In 1921, I completed all the requirements for the Degree of Doctor of Philosophy after a two years residence at the University on a University and a Grasselli Fellowship.